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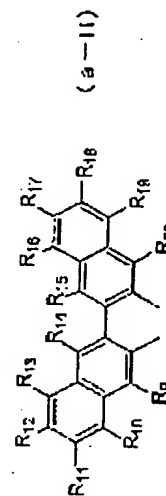
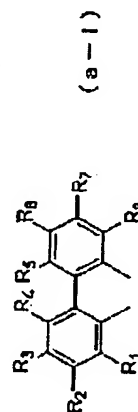
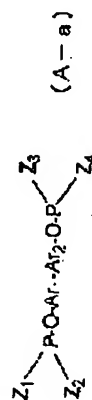
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(54) BIDENTATE PHOSPHORUS COMPOUND AND METHOD OF HYDROFORMYLATION USING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a bidentate phosphorus ligand excellent in activity, selectively, thermal stability in a hydroformylation reaction.

SOLUTION: This compound is a bidentate phosphorus compound expressed by general formula A-a. [-Ar1-Ar2- is a bisarylene group expressed by general formulas a-I or a-II; Z1 to Z4 are each a five membered heterocycle or its condensate including one or more nitrogen atoms and having nitrogen atom bonding to phosphorus atom; R4 and R5 are each independently an alkyl group, an alkoxy, a cycloalkyl, a cycloalkoxy, a silyl or siloxy group which may contain a substituent or a halogen; R1 to R3 and R6 to R8 are each independently H, an alkyl, an alkoxy, a cycloalkyl, a cycloalkoxy, a dialkyl amino, an aryl, aryloxy, an alkylaryl, an alkylaryloxy, an alkylaryloxy, arylalkyl, an arylalkoxy, cyano, hydroxy, or a halogen; R14 and R15 are each the same as the above R4 and R5; and R9 to R13 and R16 to R20 are each the same as R1 to R3 and R6 to R8)].



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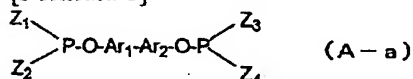
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CLAIMS

[Claim(s)]

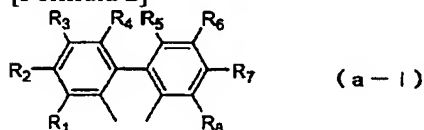
[Claim 1] 2 seat phosphorus compounds expressed with the following general formula (A-a).

[Formula 1]



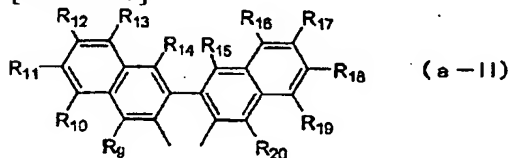
The atom which a -Ar1-Ar2-machine is the following general formula (a-I) or (a-II) a screw arylene machine with which it is expressed among [formula, and Z1 -Z4 combines with the Lynn atom is a nitrogen atom, and is the heterocyclic compound or its condensation cyclic compound of 5 member rings containing at least one nitrogen atom.

[Formula 2]



the inside of a formula, and R4 and R5 -- respectively -- independent -- an alkyl group and an alkoxy group -- A cycloalkyl machine, a cycloalkoxy machine, the silyl machine that may have the substituent, What is chosen from the group which consists of the siloxy machine and halogen atom which may have the substituent is expressed. R1-R3, and R6-R8 Independently, respectively A hydrogen atom, an alkyl group, an alkoxy group, a cycloalkyl machine, what is chosen from the group which consists of a cycloalkoxy machine, a dialkylamino machine, an aryl group, an aryloxy group, an alkyl aryl machine, an alkyl aryloxy group, an arylated-alkyl machine, an aryl alkoxy group, a cyano group, a hydroxy group, and a halogen atom is expressed

[Formula 3]

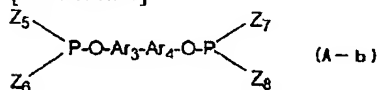


(R14 and R15 are R4 and R5, and homonymy in a general formula (a-I) independently among a formula, respectively, and R9-R13, and R16-R20 are R1-R3, R6-R8, and homonymy in a general formula (a-I) independently, respectively.)]

[Claim 2] 2 seat phosphorus compounds according to claim 1 whose -Ar1-Ar2-machine in a general formula (A-a) is a basis as which it is expressed with a general formula (a-I), and R4 and R5 are chosen from the alkyl group of carbon numbers 1-3, the alkoxy group of carbon numbers 1-3, or a halogen atom in a general formula (a-I).

[Claim 3] 2 seat phosphorus compounds expressed with the following general formula (A-b).

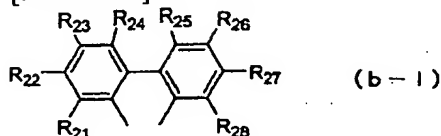
[Formula 4]



The atom which a -Ar3-Ar4-machine is the following general formula (b-I) or (b-II) a screw arylene machine with which it is expressed among [formula, and Z5 -Z8 combines with the Lynn atom is a nitrogen atom, and is the heterocyclic compound or its condensation cyclic compound of

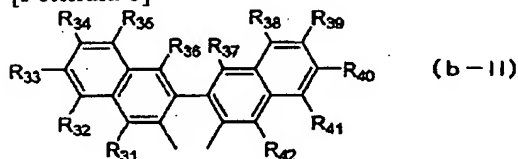
5 member rings containing at least one nitrogen atom.

[Formula 5]



the inside of a formula, and R23 and R26 -- respectively -- independent -- an alkyl group and an alkoxy group -- A cycloalkyl machine, a cycloalkoxy machine, the silyl machine that may have the substituent, What is chosen from the group which consists of the siloxy machine and halogen atom which may have the substituent is expressed. R21, R22, R24, R25, R27, and R28 Independently, respectively A hydrogen atom, an alkyl group, an alkoxy group, a cycloalkyl machine, what is chosen from the group which consists of a cycloalkoxy machine, a dialkylamino machine, an aryl group, an aryloxy group, an alkyl aryl machine, an alkyl aryloxy group, an arylated-alkyl machine, an aryl alkoxy group, a cyano group, a hydroxy group, and a halogen atom is expressed

[Formula 6]



(R34 and R39 are R23 and R26, and homonymy in a general formula (b-I) independently among a formula, respectively, and R31-R33, R35-R38, and R40-R42 are R21, and R22, R24, R25, R27, R28 and homonymy in a general formula (b-I) independently, respectively.)]

[Claim 4] 2 seat phosphorus compounds according to claim 3 whose -Ar3-Ar4-machine in a general formula (A-b) is a basis as which it is expressed with a general formula (b-I), and R23 and R26 are chosen from the alkyl group of carbon numbers 1-10, or the alkoxy group of carbon numbers 1-10 in a general formula (b-I).

[Claim 5] 2 seat phosphorus compounds according to claim 1 to 4 a general formula (A-a), and (A-b) whose inner Z1-inner Z8 are the pyrrolyl machines (pyrrolyl), indolyl machines (indolyl), or imidazolyl machines (imidazolyl) which may have the substituent respectively.

[Claim 6] A general formula (a-I), (a-II), and (b-I) (b-II) 2 seat phosphorus compounds according to claim 1 to 5 that are what sets and is chosen from the alkyl group of carbon numbers 3-20 in which R1, R8, R9, R20, R21, R28, R31, and R42 may have the substituent respectively and independently.

[Claim 7] The hydroformylation method characterized by making 2 seat phosphorus compounds according to claim 1 to 6 exist in manufacturing the aldehydes which an olefin nature compound is made to react with a carbon monoxide and hydrogen, and correspond under existence of octavus group metallic compounds.

[Claim 8] The hydroformylation method according to claim 7 in which 2 seat phosphorus compounds according to claim 1 are made to exist.

[Claim 9] The hydroformylation method according to claim 7 in which 2 seat phosphorus compounds according to claim 3 are made to exist.

[Claim 10] The hydroformylation method according to claim 7 to 9 that an olefin nature compound is a compound which does not have a polar functional group.

[Claim 11] The hydroformylation method according to claim 7 to 10 that an olefin nature compound is an alpha olefin.

[Claim 12] The hydroformylation method according to claim 7 to 11 that an olefin nature compound is a propylene.

[Claim 13] The hydroformylation method according to claim 7 to 12 that octavus group metallic compounds are rhodiums.

[Claim 14] How to manufacture alcohol by supplying a hydrogenation reaction after presenting a hydrogenation reaction with the aldehydes obtained by one method of the claims 7-13 as they are or dimerizing.

[Translation done.]

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TECHNICAL FIELD

[The technical field to which invention belongs] this invention relates to the hydroformylation method of new 2 seat phosphorus compounds and the olefin nature compound using it.

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PRIOR ART

[Description of the Prior Art] The method of making an olefin nature compound react to the bottom of existence of a catalyst with a carbon monoxide and hydrogen (water gas), and manufacturing the alcohols which are aldehydes or a hydride of those is common knowledge as the hydroformylation method. As a catalyst of a hydroformylation reaction, the fusibility complex of the 8th group metal which makes an organic phosphorous compound a ligand is usually used. Generally, the ligand used with the metal component of a catalyst does the serious influence for catalytic reaction. It is known widely that the activity and selectivity of a reaction will change with ligands a lot also in a hydroformylation reaction. In order to carry out a hydroformylation reaction advantageously industrially, improvement in reaction activity and selectivity is an important technical problem, and the design of the ligand for it is performed briskly.

[0003] Various phosphite compounds are known as a group of the phosphorus compounds used as a ligand of a hydroformylation reaction, and various phosphite compounds, such as poly phosphite which has two or more coordination nature Lynn atoms in [other than the simple monochrome phosphite like / until now / trialkyl phosphite or triaryl phosphite] a molecule, are proposed. For example, the screw phosphite compound with which at least one of two phosphite machines has a cyclic structure is indicated by JP,62-116587,A, JP,6-184036,A, and JP,11-130718,A.

[0004] On the other hand, the screw phosphite compound which two phosphite machines have not cyclized is indicated by both JP,5-178779,A, JP,10-45776,A, and JP,11-130720,A. Furthermore, it is indicated by USP5710344 that the bidentate ligand which has two Lynn atoms which have at least one P-C combination or at least one P-N combination can use it for the hydroformylation reaction of internal olefins, such as pentene acid ester.

[0005] Thus, although various phosphorus compounds were proposed as a ligand used for a hydroformylation reaction, the hydroformylation reaction using the 2 seat phosphorus compounds reported until now of the selectivity of the straight chain aldehyde which is the purpose product was inadequate when a high reaction rate was obtained, and when reverse very high straight chain selectivity was obtained, it was inadequate [reaction] in respect of the reaction rate. Furthermore, the thermal stability of the ligand itself was also inadequate.

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EFFECT OF THE INVENTION

[Effect of the Invention] The 2 seat phosphorus compounds of this invention are possible new compounds of using it as a component of a homogeneous-system metal catalyst in various organic reactions, such as hydrogenation, hydroformylation, formation of hydronalium cyano, hydronalium carboxylation, hydronalium amidation, hydronalium esterification, and aldol condensation. In this invention method, since not only high reaction activity but very high aldehyde isomer selectivity is obtained by using the 2 seat phosphorus compounds which have specific structure as a catalyst component in a hydroformylation reaction, a hydroformylation reaction can be carried out advantageously industrially.

[Translation done.]

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] Although various phosphorus compounds were conventionally proposed as a ligand used for a hydroformylation reaction as above-mentioned, since a high reaction rate and the selectivity of the high purpose product were not simultaneously filled with the hydroformylation reaction using these, it was apprehensive about bringing about the fall of economical efficiency in commercial production, and there was a problem of being hard to use as an industrial catalyst. Therefore, to give the selectivity of the outstanding purpose product and to develop a ligand with high thermal stability was desired strongly, maintaining a high reaction rate.

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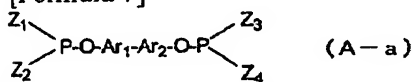
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MEANS

[Means for Solving the Problem] It is process in which examination of a ligand effective in this invention persons setting for a hydroformylation reaction, and improving and maintaining both reaction activity and selectivity of the purpose product is advanced wholeheartedly. If the new 2 seat phosphorus compounds which have specific structure are found out and this is used as a ligand used with one component of the catalyst in a hydroformylation reaction, i.e., the metal component of a catalyst It found out that the performance which the reaction advanced at a quick speed, and the selectivity of the extremely excellent purpose product was obtained, and was excellent also in thermal stability was shown, and this invention was reached. That is, the 1st summary of this invention is 2 seat phosphorus compounds expressed with the following general formula (A-a).

[0008]

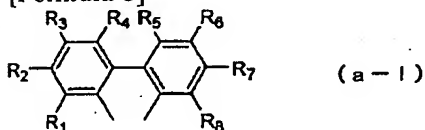
[Formula 7]



[0009] The atom which a -Ar1-Ar2-machine is the following general formula (a-I) or (a-II) a screw arylene machine with which it is expressed among [formula, and Z1 -Z4 combines with the Lynn atom is a nitrogen atom, and is the heterocyclic compound or its condensation cyclic compound of 5 member rings containing at least one nitrogen atom.

[0010]

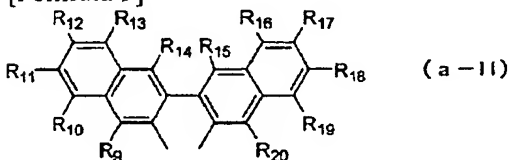
[Formula 8]



[0011] the inside of a formula, and R4 and R5 -- respectively -- independent -- an alkyl group and an alkoxy group -- A cycloalkyl machine, a cycloalkoxy machine, the silyl machine that may have the substituent, What is chosen from the group which consists of the siloxy machine and halogen atom which may have the substituent is expressed. R1-R3, and R6-R8 Independently, respectively A hydrogen atom, an alkyl group, an alkoxy group, a cycloalkyl machine, what is chosen from the group which consists of a cycloalkoxy machine, a dialkylamino machine, an aryl group, an aryloxy group, an alkyl aryl machine, an alkyl aryloxy group, an arylated-alkyl machine, an aryl alkoxy group, a cyano group, a hydroxy group, and a halogen atom is expressed

[0012]

[Formula 9]

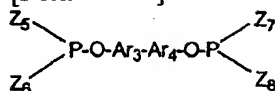


[0013] (R14 and R15 are R4 and R5, and homonymy in a general formula (a-I) independently among a formula, respectively, and R9-R13, and R16-R20 are R1-R3, R6-R8, and homonymy in a general formula (a-I) independently, respectively.) It consists in].

[0014] Moreover, the 2nd summary of this invention is 2 seat phosphorus compounds expressed with the following general formula (A-b).

[0015]

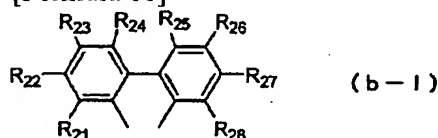
[Formula 10]



[0016] The atom which a -Ar3-Ar4-machine is the following general formula (b-I) or (b-II) a screw arylene machine with which it is expressed among [formula, and Z5 -Z8 combines with the Lynn atom is a nitrogen atom, and is the heterocyclic compound or its condensation cyclic compound of 5 member rings containing at least one nitrogen atom.

[0017]

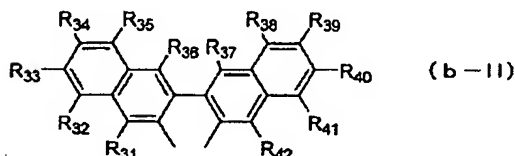
[Formula 11]



[0018] the inside of a formula, and R23 and R26 -- respectively -- independent -- an alkyl group and an alkoxy group -- A cycloalkyl machine, a cycloalkoxy machine, the silyl machine that may have the substituent, What is chosen from the group which consists of the siloxy machine and halogen atom which may have the substituent is expressed. R21, R22, R24, R25, R27, and R28 Independently, respectively A hydrogen atom, an alkyl group, an alkoxy group, a cycloalkyl machine, what is chosen from the group which consists of a cycloalkoxy machine, a dialkylamino machine, an aryl group, an aryloxy group, an alkyl aryl machine, an alkyl aryloxy group, an arylated-alkyl machine, an aryl alkoxy group, a cyano group, a hydroxy group, and a halogen atom is expressed

[0019]

[Formula 12]



[0020] (R34 and R39 are R23 and R26, and homonymy in a general formula (b-I) independently among a formula, respectively, and R31-R33, R35-R38, and R40-R42 are R21, and R22, R24, R25, R27, R28 and homonymy in a general formula (b-I) independently, respectively.) It consists in]

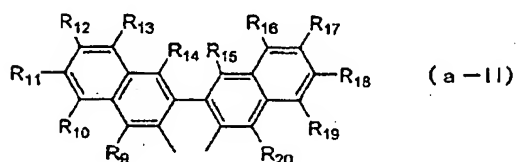
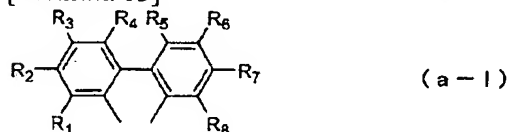
[0021] Moreover, in case the 3rd summary of this invention manufactures the aldehydes which an olefin nature compound is made to react with a carbon monoxide and hydrogen, and correspond under existence of the 8th group metallic compounds, it consists in the hydroformylation method characterized by making 2 seat phosphorus compounds according to claim 1 to 6 exist.

[0022]

[Embodiments of the Invention] this invention is explained still in detail below. the new 2 seat phosphorus compounds (A-a) of this invention -- more -- concrete -- the -Ar1-Ar2-machine -- the following general formula (a-I) -- or (a-II) it is expressed

[0023]

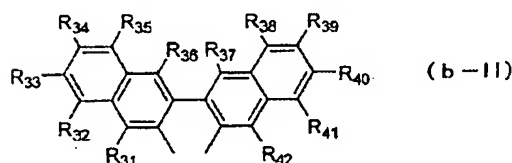
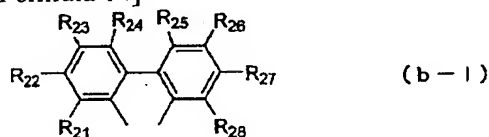
[Formula 13]



[0024] Or (a-II) it sets. the above-mentioned formula (a-I) -- R4, R5, R14, and R15 For example, a methyl group, an ethyl group, n-propyl group, an isopropyl machine, t-butyl, The straight chain of the carbon numbers 1-12, such as a decyl group, or the alkyl group of branching, a cyclo propyl group, The cycloalkyl machine of the carbon numbers 3-12, such as a cyclohexyl machine, a methoxy machine, Halogen atoms, such as siloxy machines, such as silyl machines, such as an alkoxy group of the carbon numbers 1-12, such as an ethoxy basis and a t-butoxy machine, and a trimethylsilyl machine, and a trimethylsiloxy machine, a chlorine atom, a fluorine atom, a bromine atom, and an iodine atom, are illustrated. Halogen atoms, such as a lower alkoxy group of the carbon numbers 1-3, such as a low-grade alkyl group of the carbon numbers 1-3, such as a methyl group and an ethyl group, a methoxy machine, and an ETOSHIKI machine, and a chlorine atom, are desirable, and a methyl group and especially a methoxy machine are [among these] desirable. Moreover, as a substituent of a silyl machine or a siloxy machine, the alkyl group of carbon numbers 1-3 or the alkoxy group of carbon numbers 1-3 is desirable. R1-R3 of (a-I), R6-R8 and R9-R13 of a formula (a-II), and R16-R20 [moreover,] An ethyl group, others, for example, a methyl group, n-propyl group, i-propyl group, [hydrogen atom] n-butyl, s-butyl, t-butyl, n-pentyl machine, an isopentyl machine, The alkyl group of the carbon numbers 1-20, such as a neopentyl machine, t-pentyl machine, and t-hexyl machine The cycloalkyl machine of the carbon numbers 3-20, such as a cyclohexyl machine, a cyclo octyl machine, and an adamantyl machine The aryl group of the carbon numbers 6-20, such as a phenyl group and a naphthyl group, a methoxy machine, The alkoxy group of the carbon numbers 1-12, such as an ethoxy basis, an isopropoxy group, and a t-butoxy machine The dialkylamino machine of the carbon numbers 2-20, such as a dimethylamino machine and a diethylamino machine The aryloxy group of the carbon numbers 6-20, such as a phenoxy machine and a naphthoxy machine The arylated-alkyl machine of the carbon numbers 7-20, such as a benzyl, p-tolyl group, The cycloalkoxy machine of the carbon numbers 3-20, such as a cyclopenthyloxy machine besides the alkyl aryl machine of the carbon numbers 7-20, such as o-tolyl group The alkyl aryloxy group of the carbon numbers 7-20, such as 2 and 3-KISHIRENOKISHI Halogen atoms, such as the aryl alkoxy group of the carbon numbers 7-20, such as a 2-(2-naphthyl) ethoxy basis, a cyano group, a hydroxy group, a fluoro machine, a chloro machine, and a BUROMO machine, etc. are mentioned, and even if respectively the same, you may differ. A formula (a-I) as a thing suitable as a screw arylene machine which reaches (a-II) 3 and 3'-G t-butyl -5, 5', 6, and 6'-tetramethyl - The 1 and 1'-biphenyl -2, a 2'-diyl machine, 3, 3', 5, and 5'-tetrapod-t-butyl -6, the 6'-dimethyl -1, the 1'-biphenyl -2, a 2'-diyl machine, The 3, 3', 5, and 5'-tetrapod-t-pentyl -6, the 6'-dimethyl -1, the 1'-biphenyl -2, a 2'-diyl machine, The 3, 3', 5, and 5'-tetrapod-t-hexyl -6, the 6'-dimethyl -1, the 1'-biphenyl -2, a 2'-diyl machine, 3 and 3'-G t-butyl -5, 5'-dimethoxy -6, the 6'-dimethyl -1, the 1'-biphenyl -2, a 2'-diyl machine, 3 and 3'-G t-butyl -5, 5'-diethoxy -6, the 6'-dimethyl -1, the 1'-biphenyl -2, a 2'-diyl machine, 3 and 3'-G t-butyl -5, 5'-diethoxy -6, the 6'-dimethyl -1, the 1'-biphenyl -2, a 2'-diyl machine, 3 and 3'-G t-butyl -5, 5'-G t-butoxy - The 6 and 6'-dimethyl -1, the 1'-biphenyl -2, a 2'-diyl machine, 3, 3', 5, and 5'-tetrapod (cyclo octyl) -6, 6'-dimethyl -1, 1'-biphenyl -2, 2'-diyl machine, 3, 3', 5, and 5'-tetrapod-t-butyl -6, 6'-dichloro -1, the 1'-biphenyl -2, a 2'-diyl machine, etc. are mentioned.

[0025] moreover, another new 2 seat phosphorus compounds (A-b) of this invention -- more -- concrete -- the -Ar3-Ar4-machine -- the following general formula (b-I) -- or (b-II) it is expressed [0026]

[Formula 14]



[0027] the above-mentioned formula (b-I) -- and (b-II) they express the alkyl group of the straight chain of the carbon numbers 1-10, such as n-propyl group, i-propyl group, s-butyl, t-butyl, an

isopentyl machine, a neopentyl machine, t-pentyl machine, and t-hexyl machine, or branched chain, especially, it sets and especially the thing of carbon numbers 4-10 is [R23, R26, R34, and R39 have the desirable thing of carbon numbers 3-10 Furthermore, the carbon atom combined with a ring has the desirable thing of the 3rd class, and t-butyl, t-pentyl machine, t-hexyl machine, etc. are illustrated. moreover -- in addition to this -- carbon numbers 1-10 -- desirable -- the carbon numbers 6-14, such as an alkoxy group of 1-5, a cyclohexyl machine, a cyclo octyl machine, and an adamantyl machine, -- halogen atoms, such as siloxy machines, such as silyl machines, such as a cycloalkyl machine of 6-10 and a trimethylsilyl machine, and a trimethylsiloxy machine, a chlorine atom, a fluorine atom, a bromine atom, and an iodine atom, are mentioned preferably The substituent of a silyl machine or a siloxy machine has the alkyl group of carbon numbers 1-3, or the desirable alkoxy group of carbon numbers 1-3. R21, R22, R24, R25, R27 and R28 of (b-I) and R31-R33 of a formula (b-II), R35-R38, and R40-R42 [moreover,] An ethyl group, others, for example, a methyl group, n-propyl group, i-propyl group, [hydrogen atom] n-butyl, s-butyl, t-butyl, n-pentyl machine, an isopentyl machine, The alkyl group of the carbon numbers 1-20, such as a neopentyl machine, t-pentyl machine, and t-hexyl machine The cycloalkyl machine of the carbon numbers 3-20, such as a cyclohexyl machine, a cyclo octyl machine, and an adamantyl machine The aryl group of the carbon numbers 6-20, such as a phenyl group and a naphthyl group, a methoxy machine, The alkoxy group of the carbon numbers 1-12, such as an ethoxy basis, an isopropoxy group, and a t-butoxy machine The dialkylamino machine of the carbon numbers 2-20, such as a dimethylamino machine and a diethylamino machine The aryloxy group of the carbon numbers 6-20, such as a phenoxy machine and a naphthoxy machine The arylated-alkyl machine of the carbon numbers 7-20, such as a benzyl, p-tolyl group, The cycloalkoxy machine of the carbon numbers 3-20, such as a cyclopenthyloxy machine besides the alkyl aryl machine of the carbon numbers 7-20, such as o-tolyl group The alkyl aryloxy group of the carbon numbers 7-20, such as 2 and 3-KISHIRENOKISHI Halogen atoms, such as the aryl alkoxy group of the carbon numbers 7-20, such as a 2-(2-naphthyl) ethoxy basis, a cyano group, a hydroxy group, a fluoro machine, a chloro machine, and a BUROMO machine, etc. are mentioned, and even if respectively the same, you may differ.

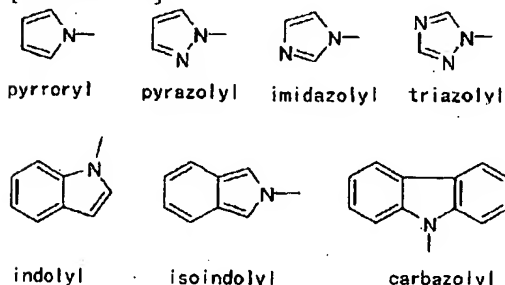
[0028] A formula (b-I) as a thing suitable as a screw arylene machine which reaches (b-II) 3 and 3'-G t-butyl -5, the 5'-dimethyl -1, the 1'-biphenyl -2, a 2'-diyl machine, 3, 3', 5, and 5'-tetrapod-t-butyl -1, the 1'-biphenyl -2, a 2'-diyl machine, The 3, 3', 5, and 5'-tetrapod-t-pentyl -1, the 1'-biphenyl -2, a 2'-diyl machine, The 3, 3', 5, and 5'-tetrapod-t-hexyl -1, the 1'-biphenyl -2, a 2'-diyl machine, 3 and 3'-G t-butyl -5, 5'-dimethoxy -1, the 1'-biphenyl -2, a 2'-diyl machine, 3 and 3'-G t-butyl -5, 5'-diethoxy -1, the 1'-biphenyl -2, a 2'-diyl machine, 3 and 3'-G t-butyl -5, 5'-G t-butoxy -1, The 1 and 1'-biphenyl -2, 2'-diyl machine, 3, 3', 5, and 5'-tetrapod (cyclo octyl) -1, the 1'-biphenyl -2, a 2'-diyl machine, etc. are mentioned.

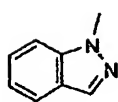
[0029] As R1 and R8 of a general formula (a-I), R9 and R20 of a general formula (a-II), R21 and R28 of a general formula (b-I), and R31 and R34 of a general formula (b-II) When the thermal stability of 2 seat phosphorus compounds is high and uses as a ligand of a hydroformylation catalyst also in the substituent mentioned above The alkyl group of the straight chain of carbon numbers 3-20 or branched chain is desirable, the alkyl group of carbon numbers 4-18 is still more desirable especially, and especially the alkyl group of the letter of branching of carbon numbers 4-8 is desirable at the point that high activity and high selectivity are shown.

[0030] The Lynn atom and the atom to combine are nitrogen atoms, and at least one Z1 -Z8 in a formula (A-a) and a formula (A-b) is the heterocyclic compound or its condensation cyclic compound of 5 member rings which usually contain 1-4 nitrogen atoms [1-3] preferably. As Z1-Z8, especially, it is desirable that it is the heterocyclic compound of 5 member rings containing one nitrogen atom, and a pyrrole is especially desirable. What was shown below is mentioned as an example of Z1-Z8.

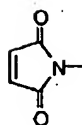
[0031]

[Formula 15]

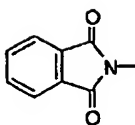




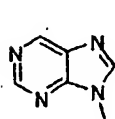
indazolyl



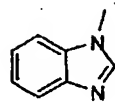
maleimidyl



phthalimidyl



purinyl



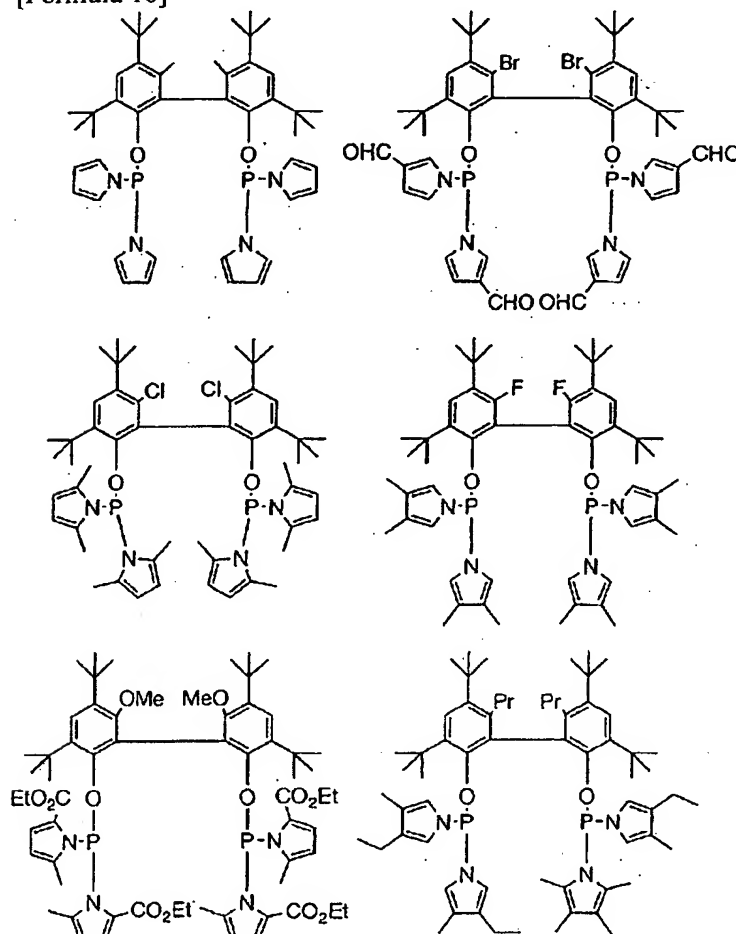
benzimidazolyl

[0032] Z1 -Z8 may have the substituent further. as a substituent A methyl group, an ethyl group, n-propyl group, i-propyl group, n-butyl, s-butyl, t-butyl, n-pentyl machine, an isopentyl machine, a neopentyl machine, the carbon numbers 1-12, such as t-pentyl machine, -- desirable -- the alkyl group of the straight chain of 1 - 8**, or branched chain -- the carbon numbers 1-12, such as a methoxy machine and an ethoxy basis, -- desirable -- the alkoxy group of 1 - 8** -- The aryl group of 6-10 etc. is mentioned preferably. the carbon numbers 6-18, such as a phenyl group and a naphthyl group, -- A halogen atom, a cyano group, a nitro group, a triffe RUORU methyl group, a hydroxyl, the amino group, an acyl group, carbonyloxy group, an oxy-carbonyl group, an amide group, a sulfonyl machine, a sulfinyl machine, a silyl machine, a thionyl machine, etc. are mentioned to others. 1-5 of these substituents may be replaced to one Z.

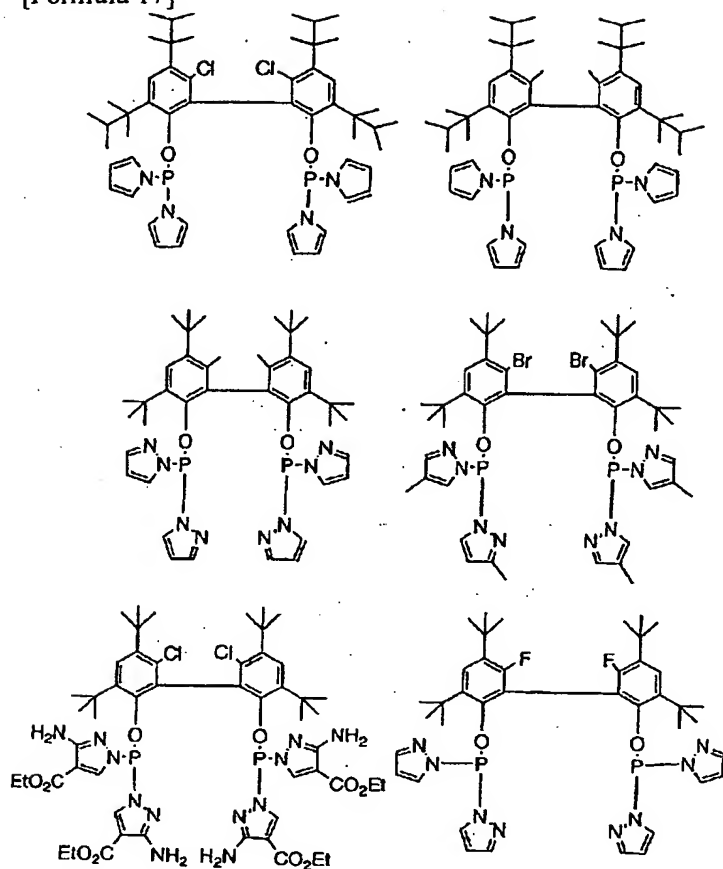
[0033] The above-mentioned general formula (A-a) and (A-b) the example of 2 seat phosphorus compounds expressed are shown below.

[0034]

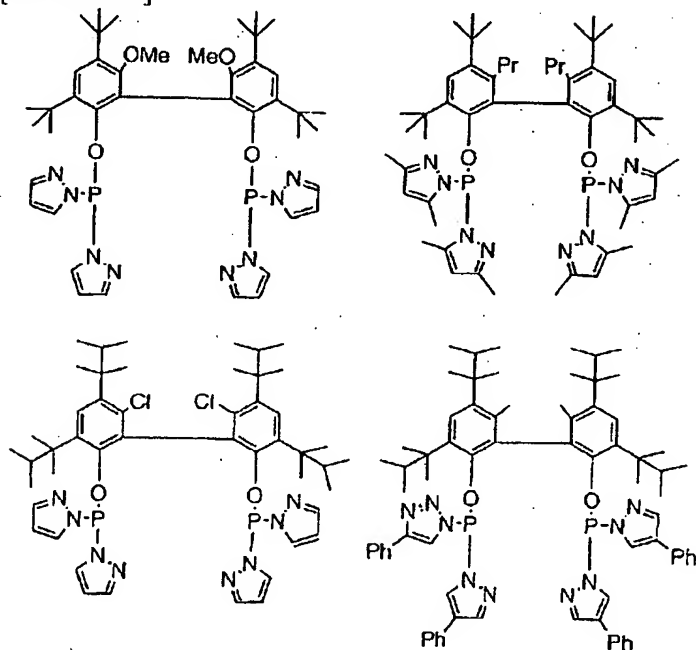
[Formula 16]

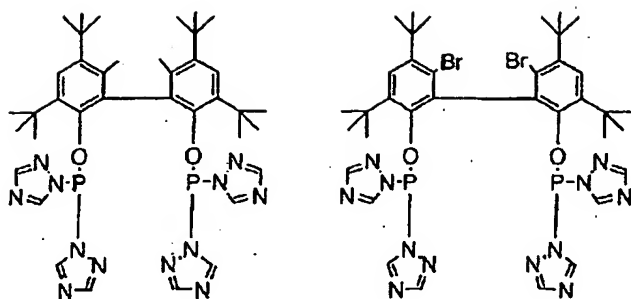


[0035]
[Formula 17]

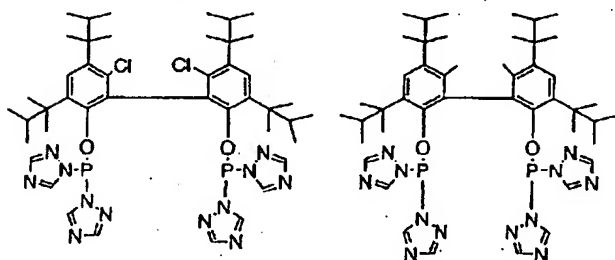
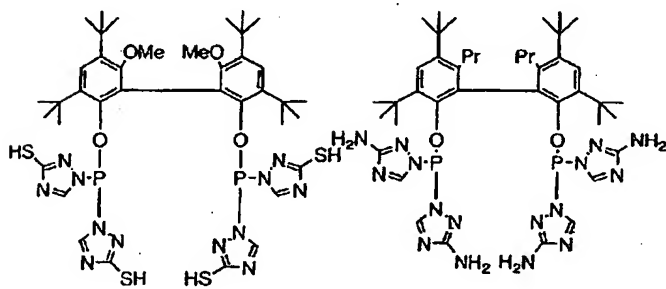
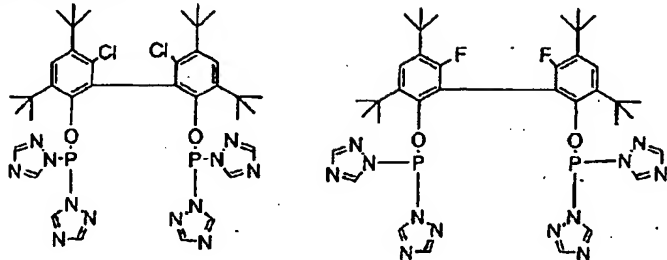


[0036]
[Formula 18]

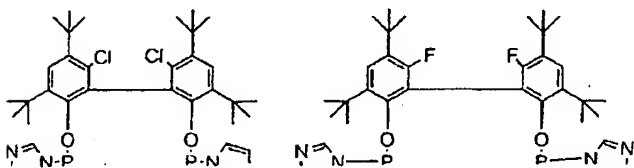
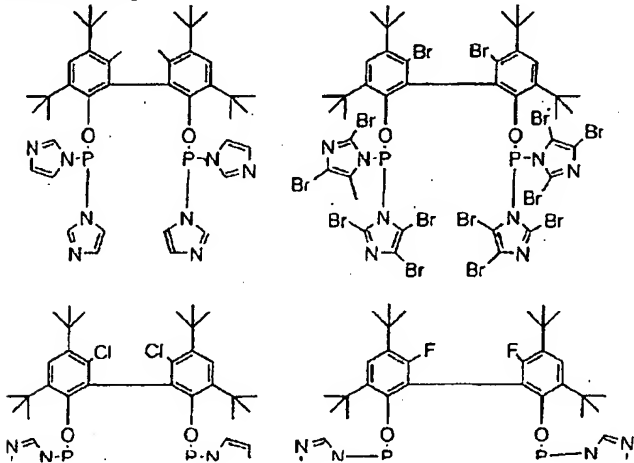


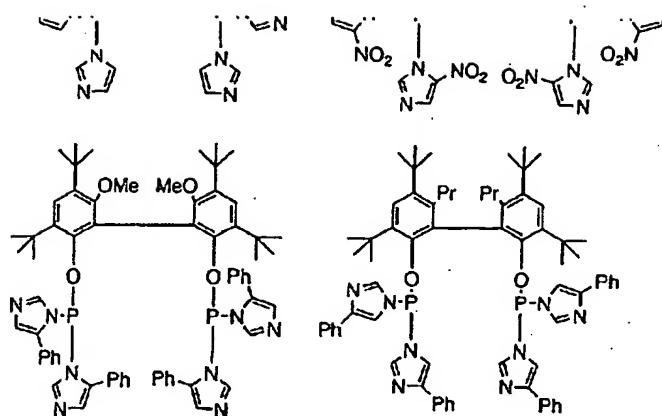


[0037]
[Formula 19]

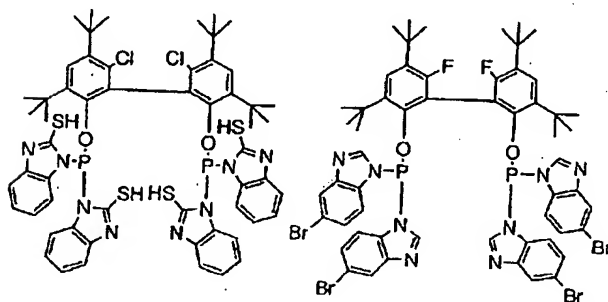
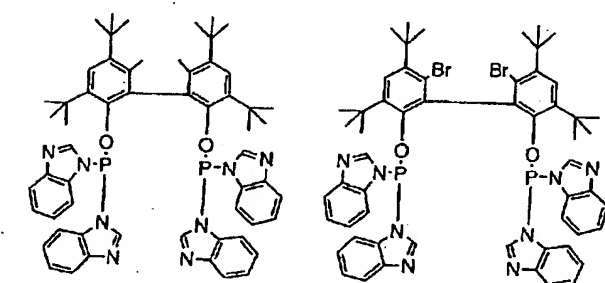
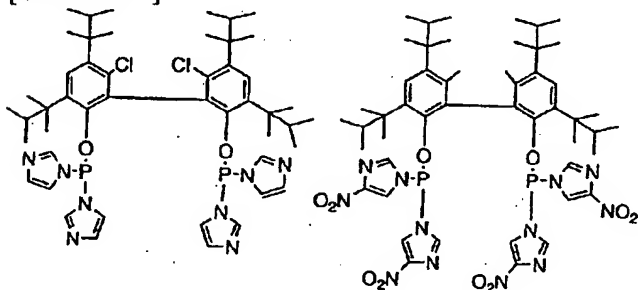


[0038]
[Formula 20]

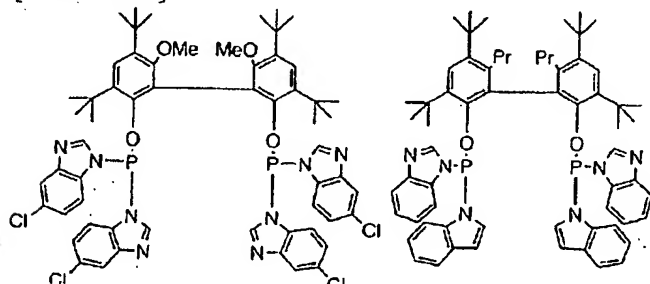


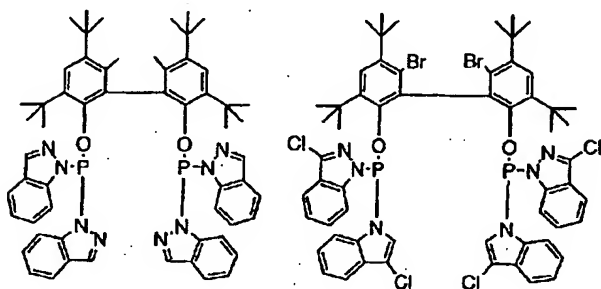
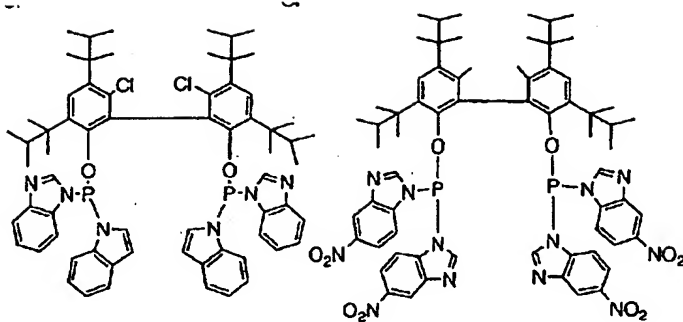


[0039]
[Formula 21]

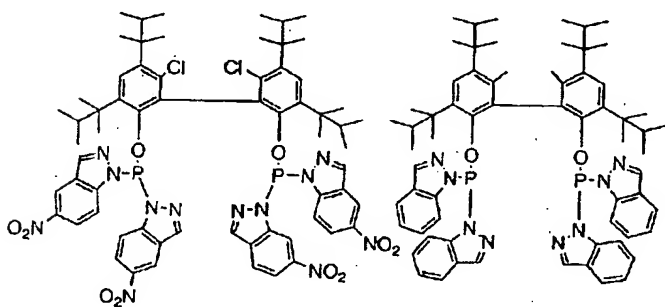
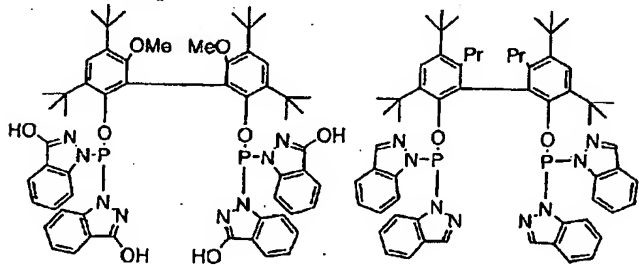
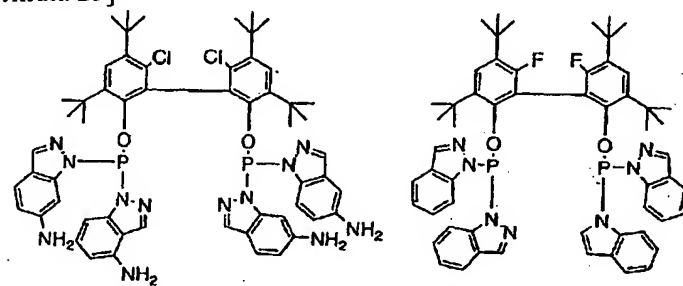


[0040]
[Formula 22]

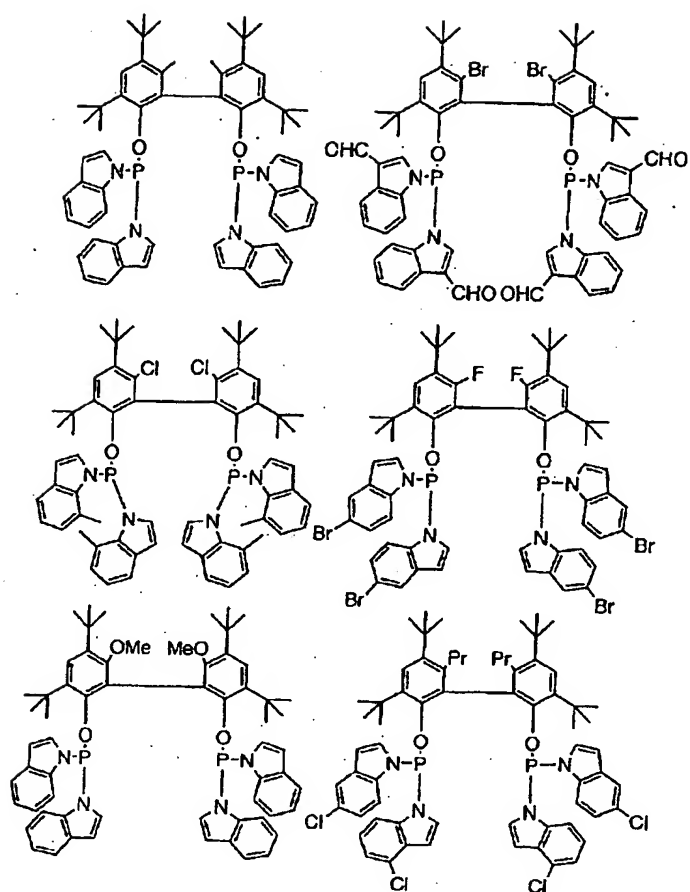




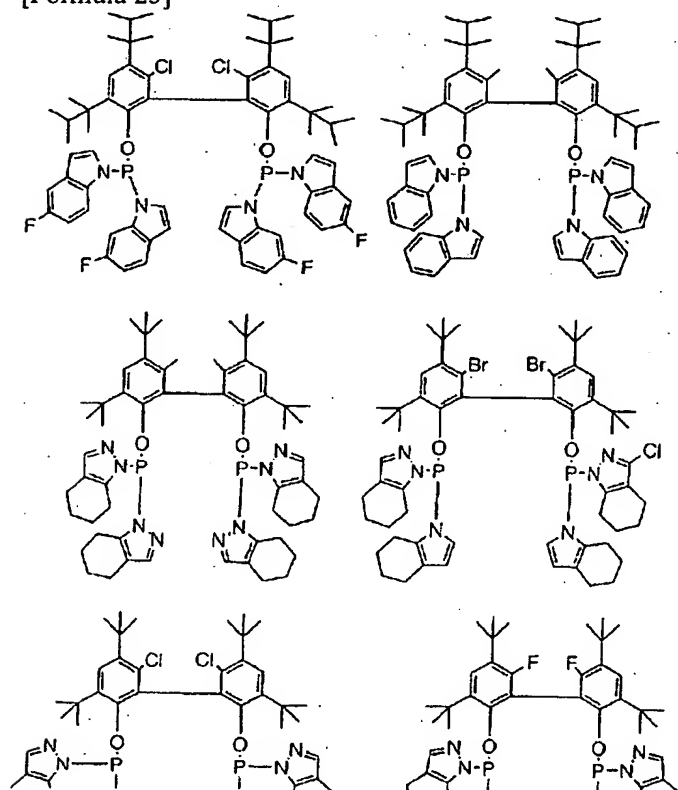
[0041]
[Formula 23]

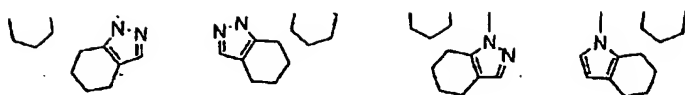


[0042]
[Formula 24]

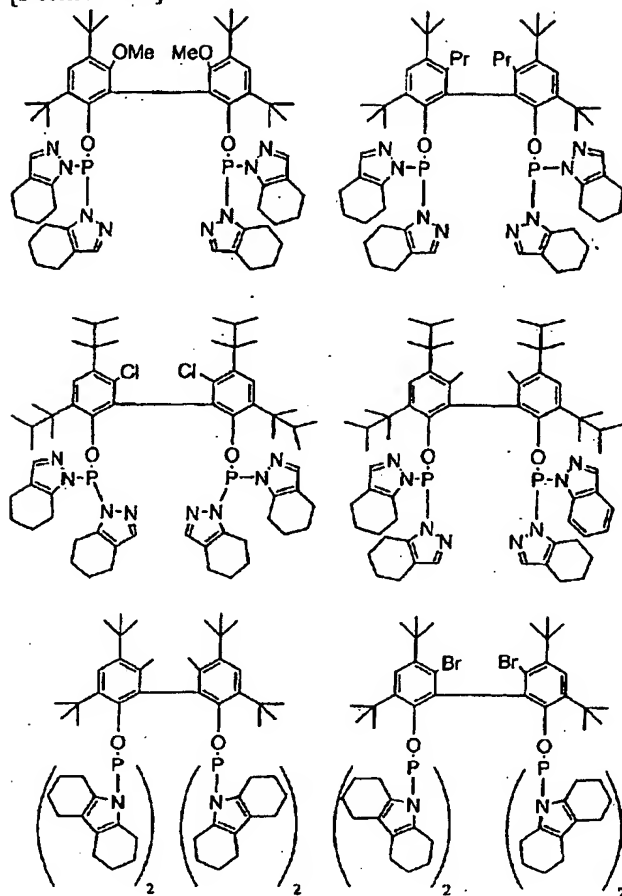


[0043]
[Formula 25]

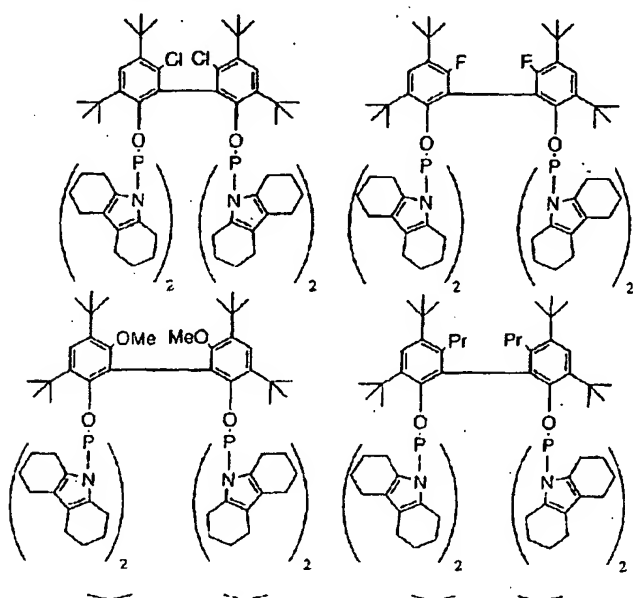


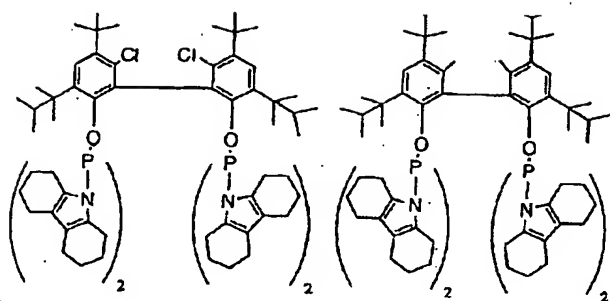


[0044]
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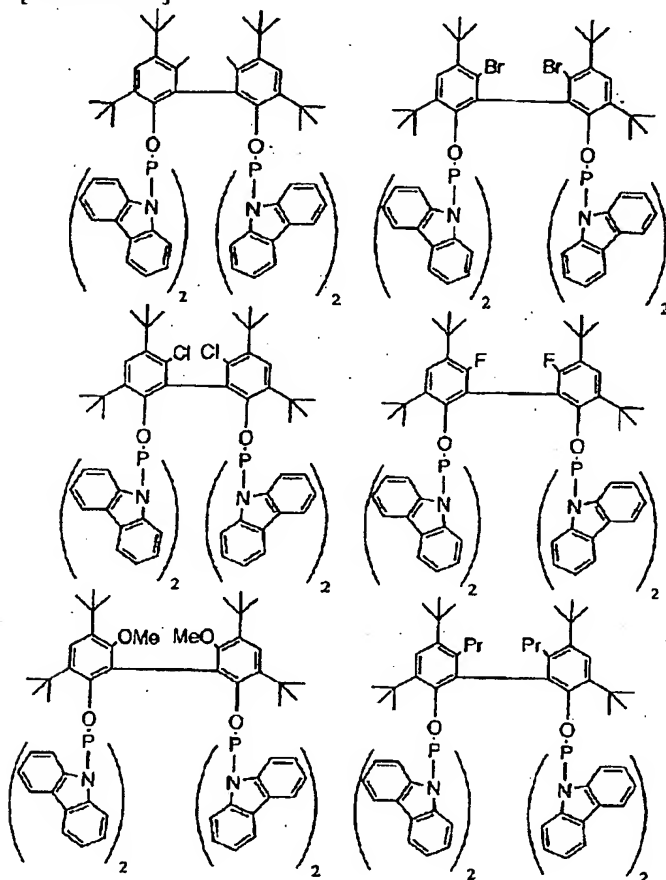


[0045]
[Formula 27]

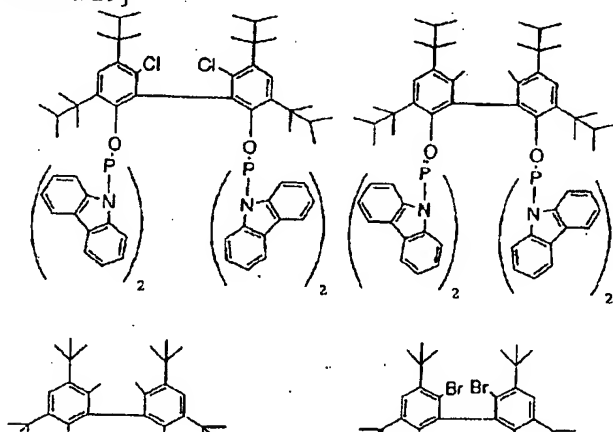


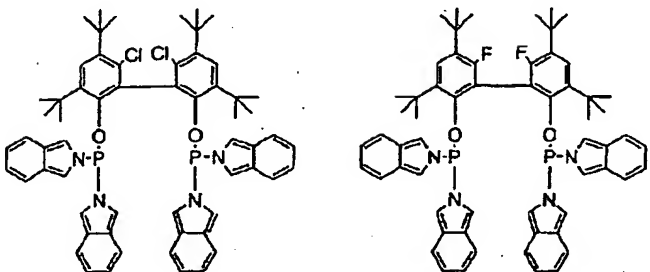
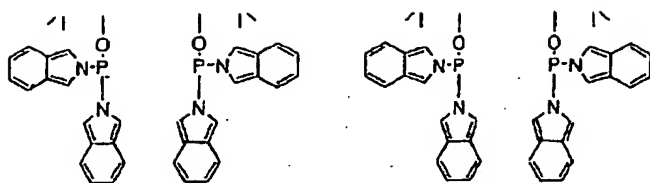


[0046]
[Formula 28]

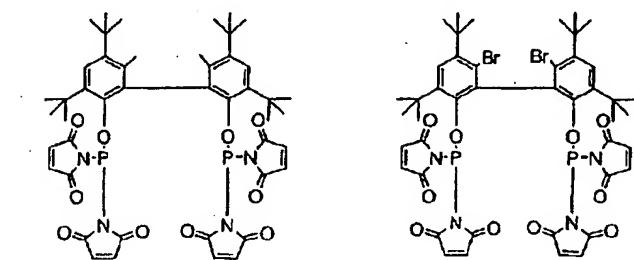
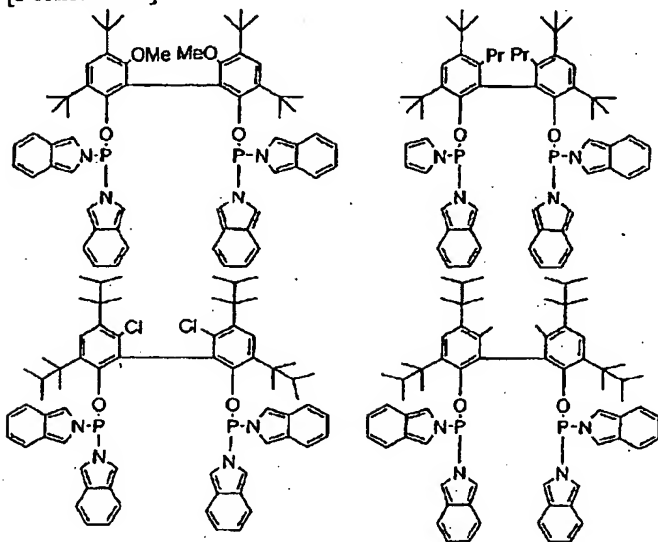


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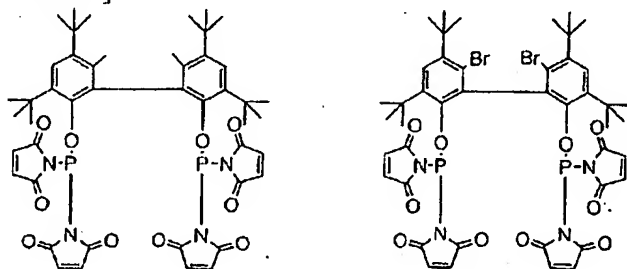


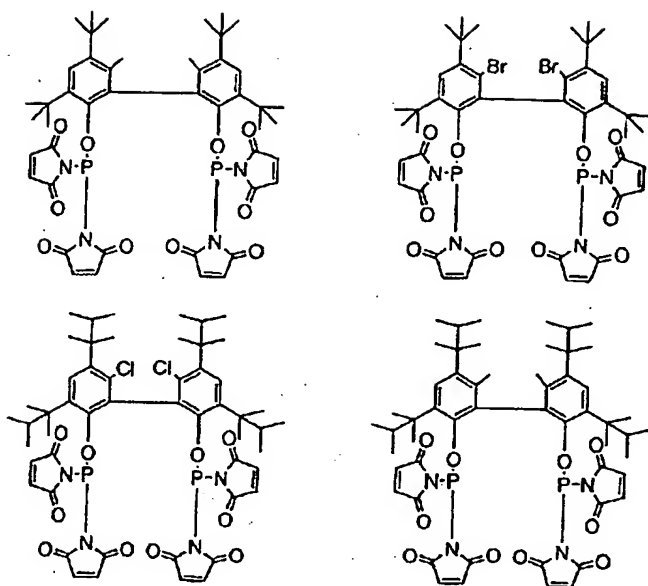


[0048]
[Formula 30]

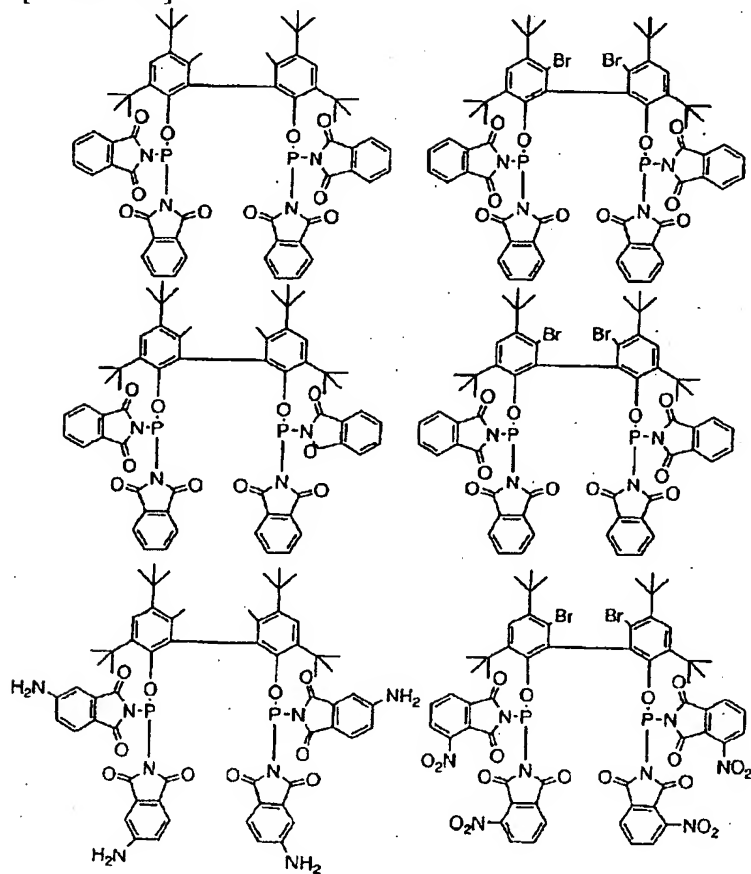


[0049]
[Formula 31]

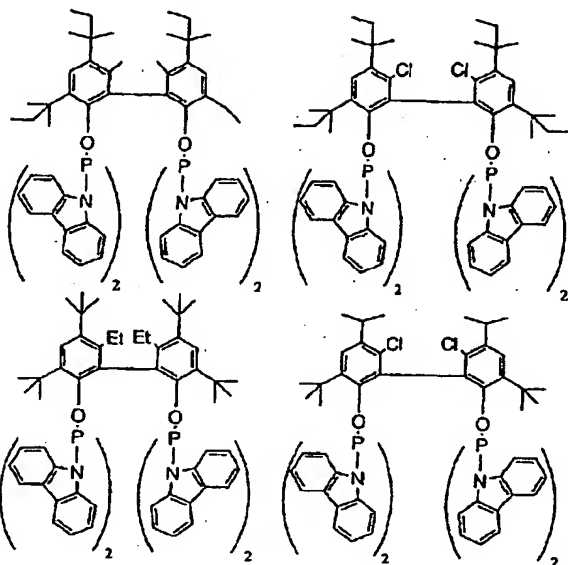
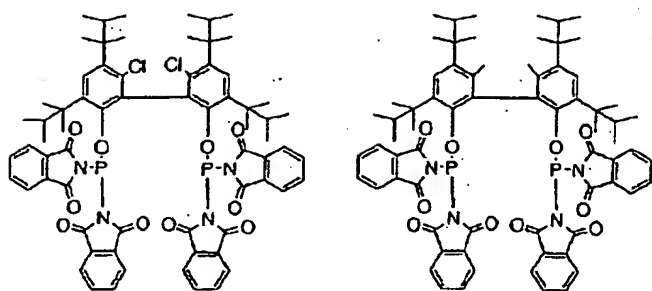




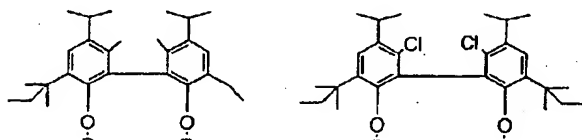
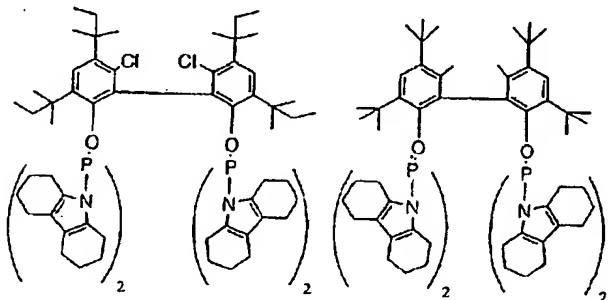
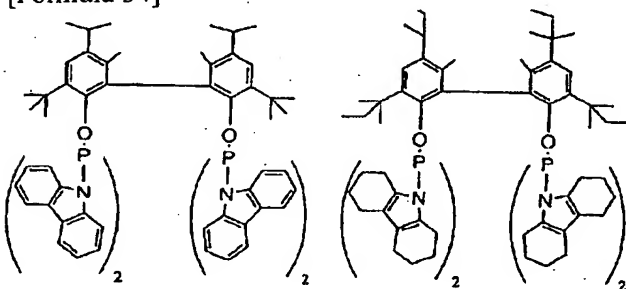
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[Formula 32]

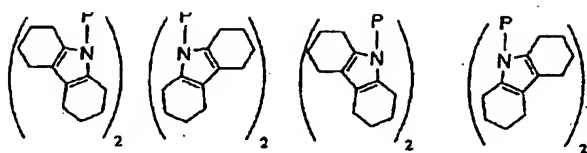


[0051]
[Formula 33]

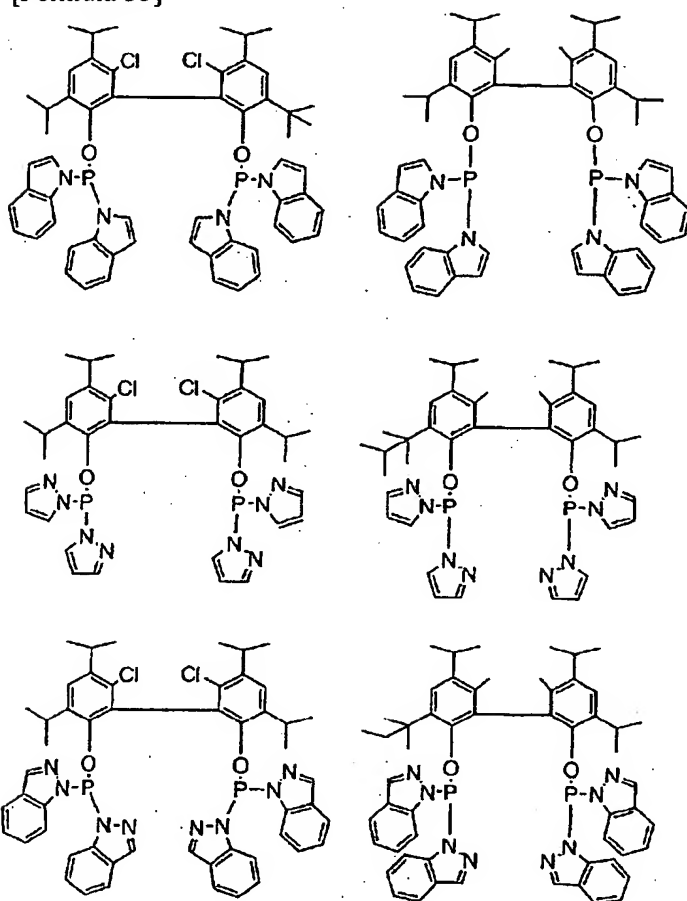


[0052]
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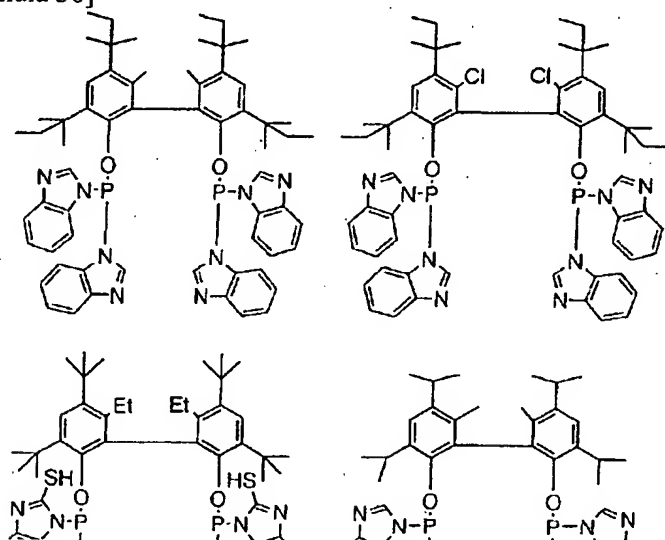


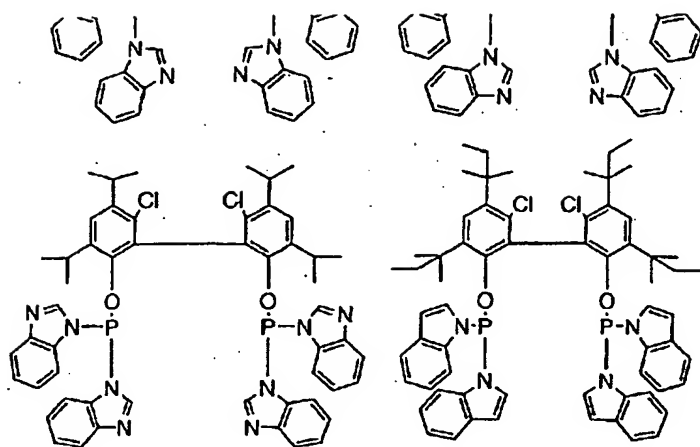


[0053]
[Formula 35]

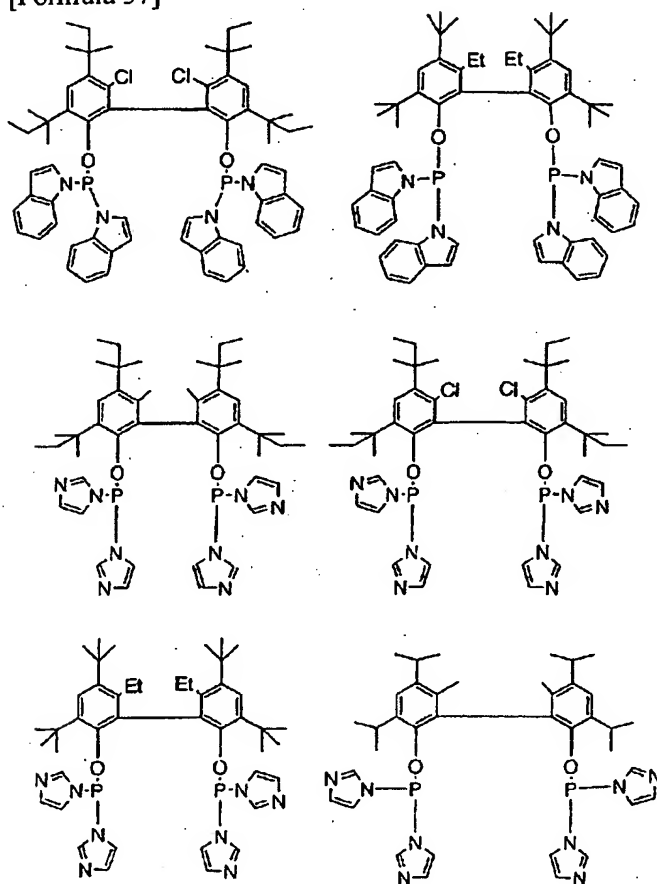


[0054]
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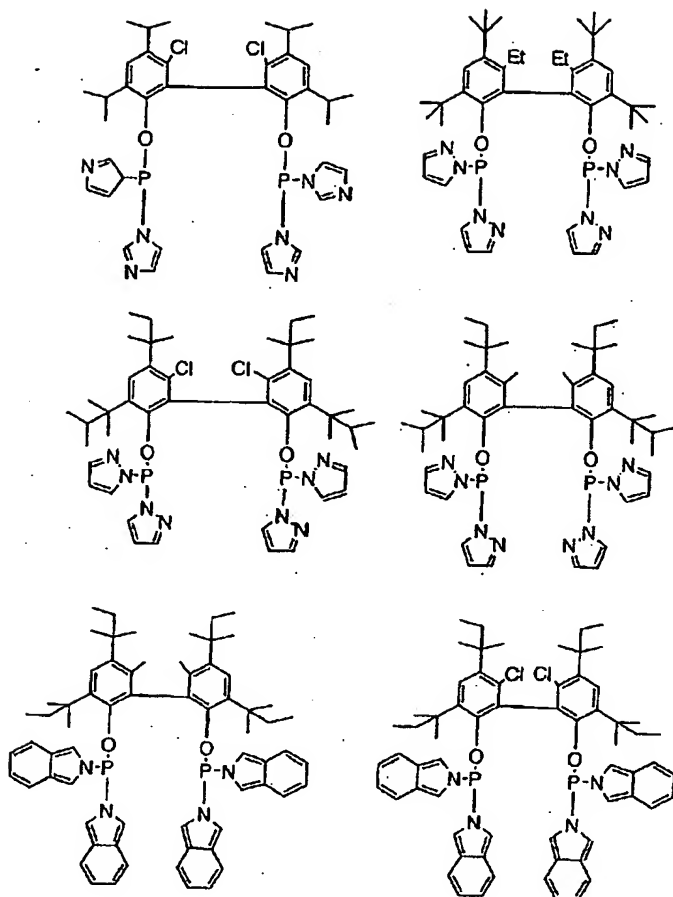




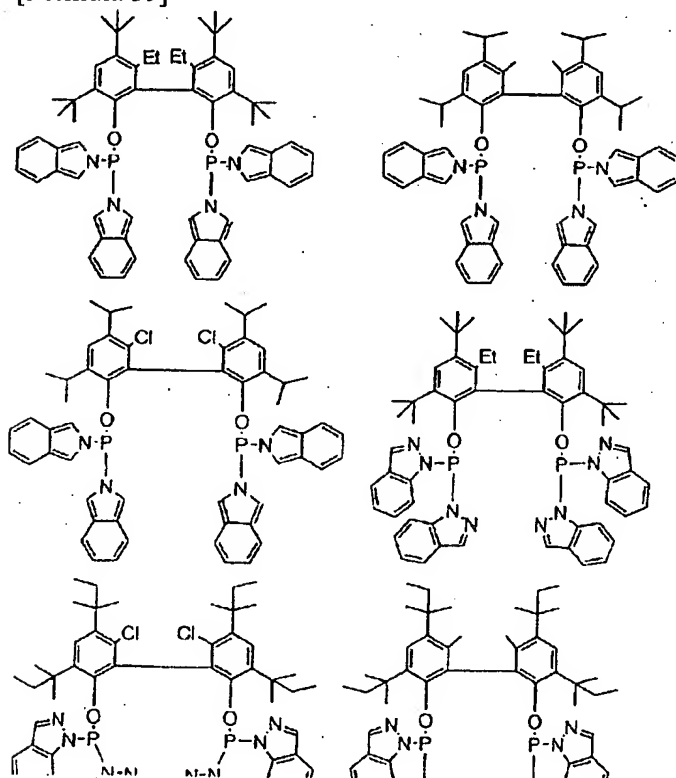
[0055]
[Formula 37]

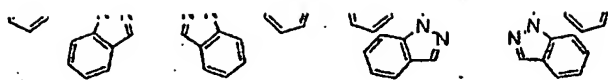


[0056]
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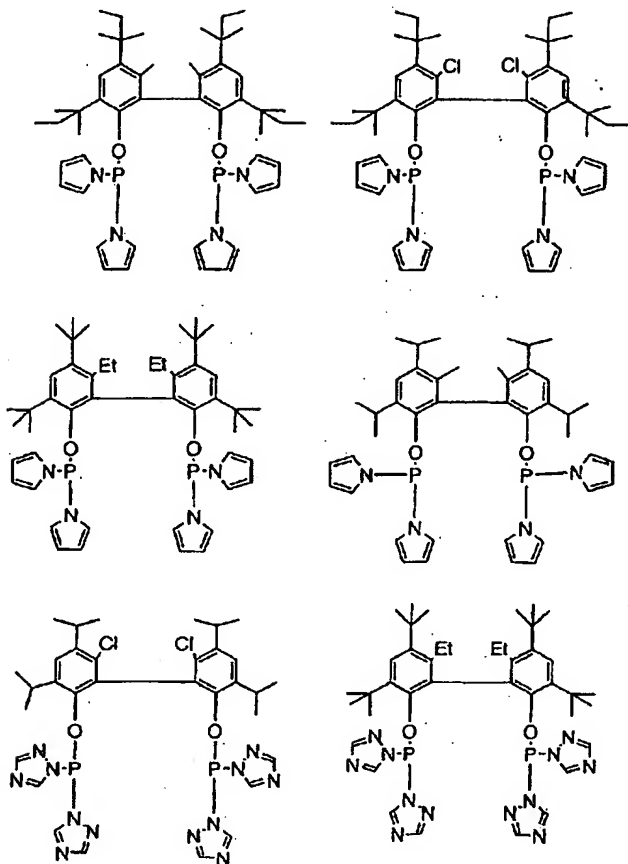


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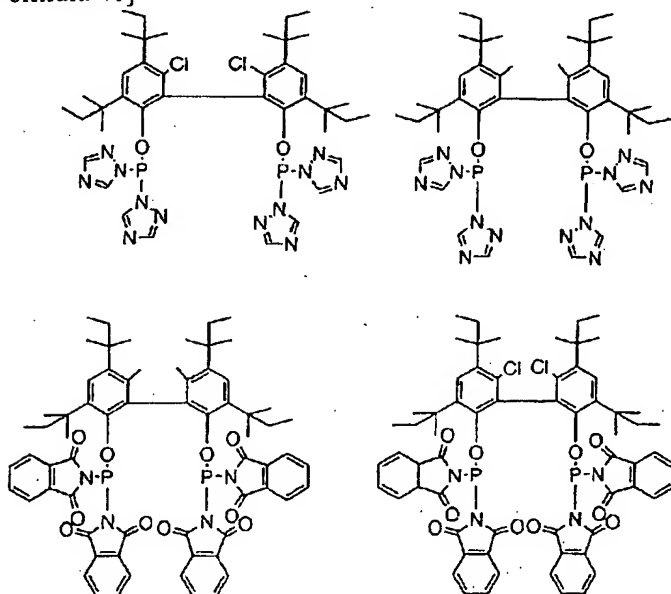


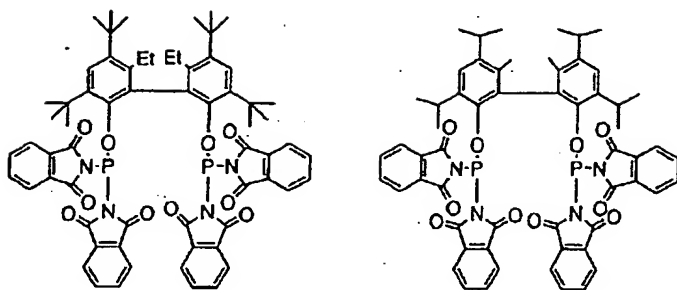


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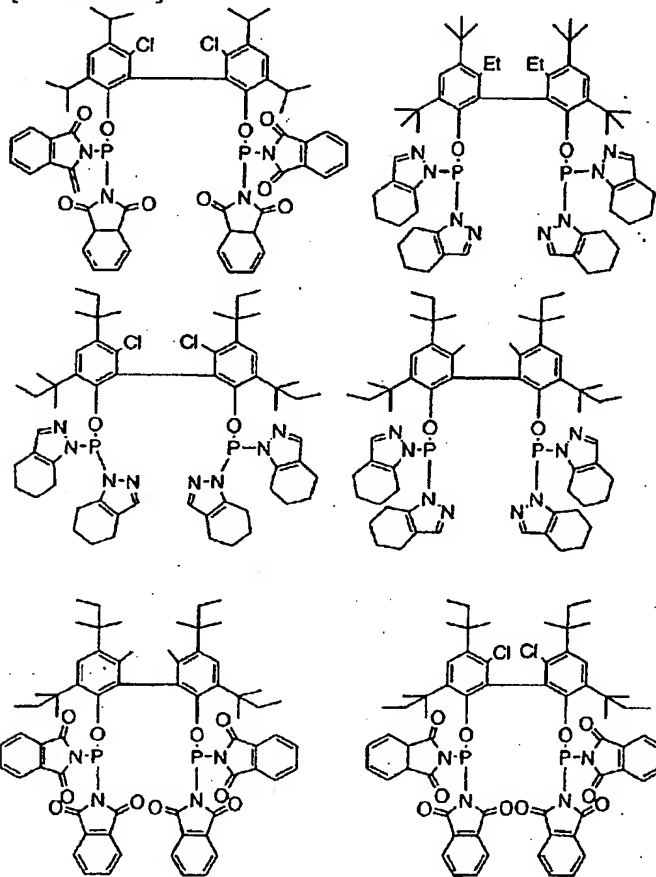


[0059]
[Formula 41]

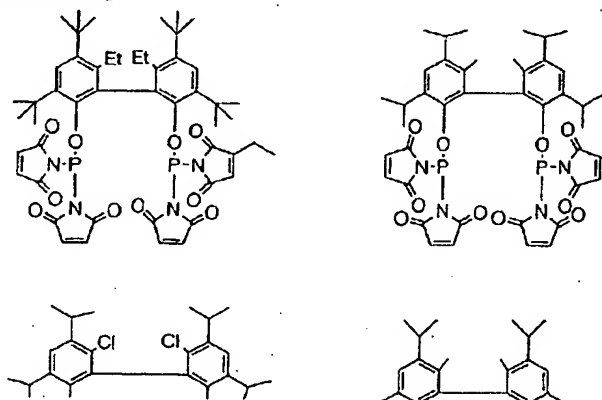


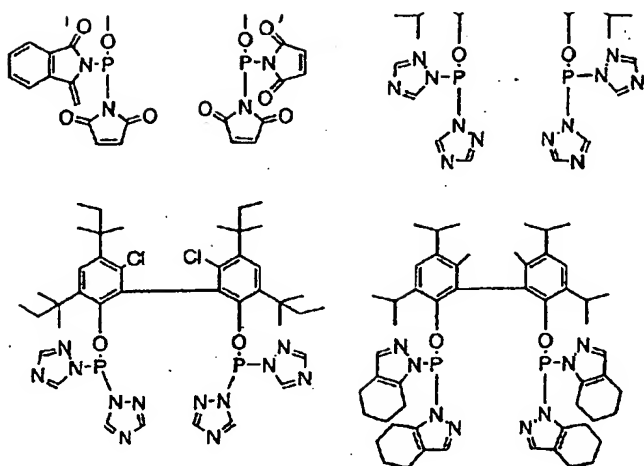


[0060]
[Formula 42]

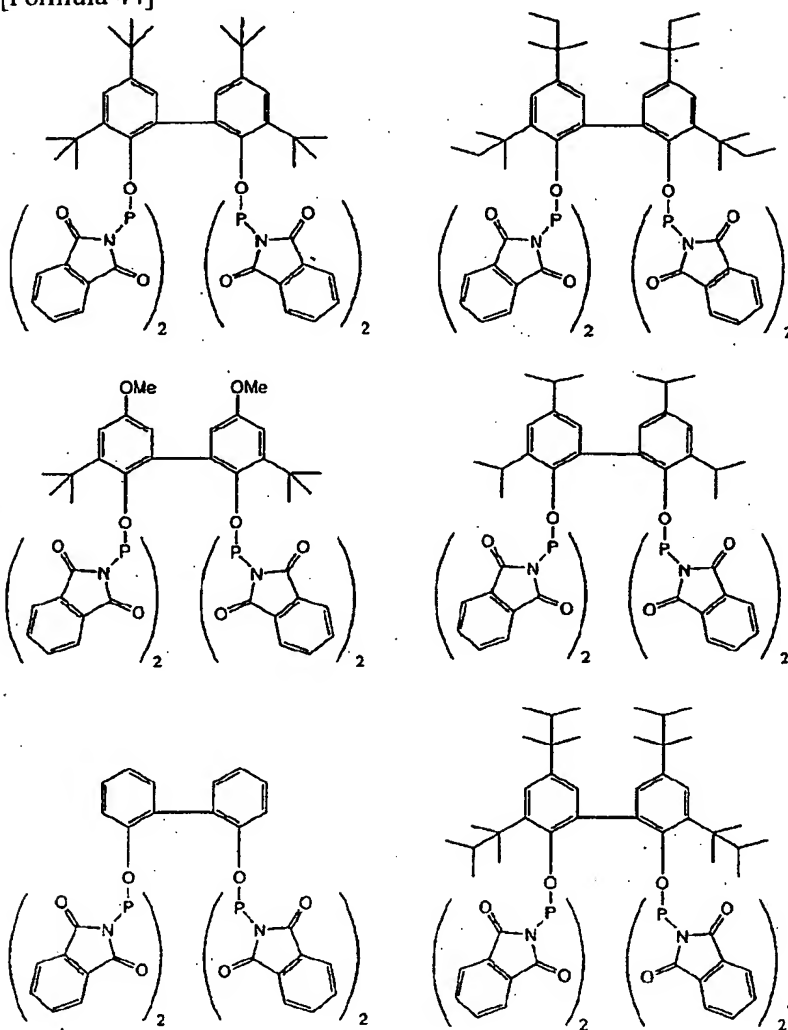


[0061]
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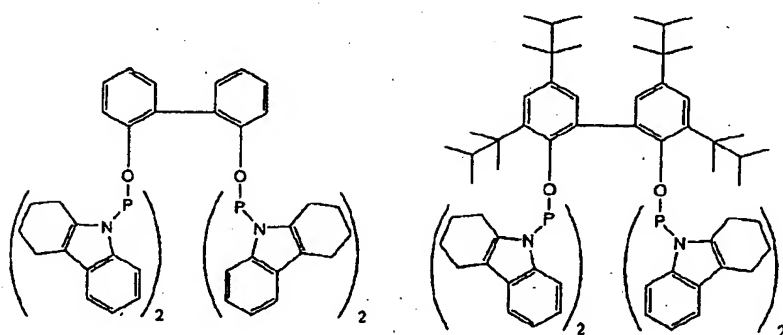
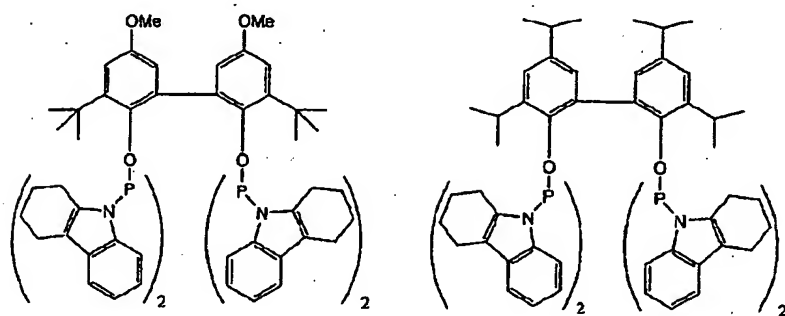
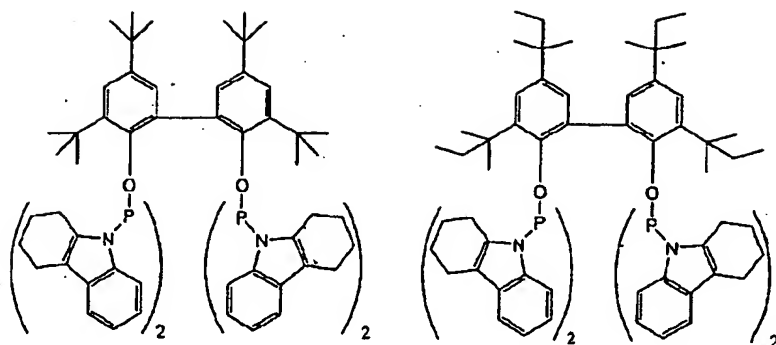




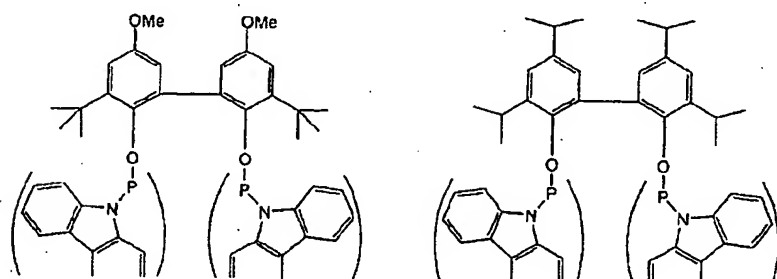
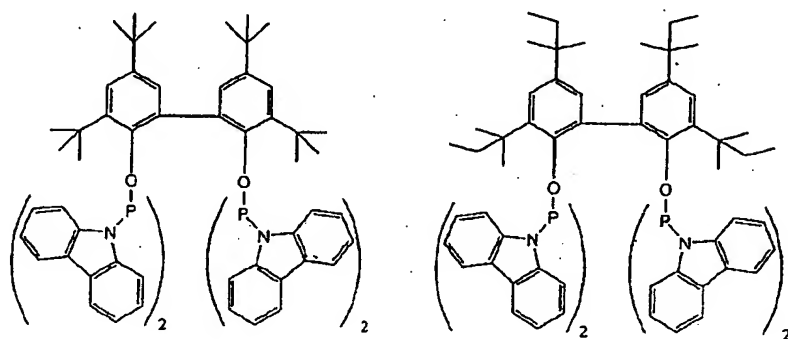
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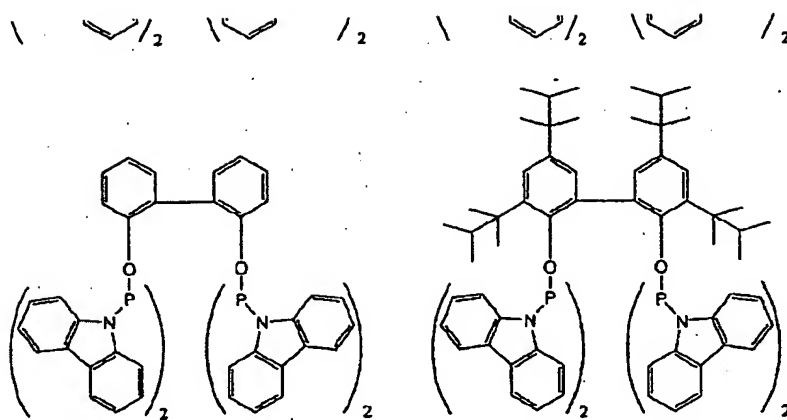


[0063]
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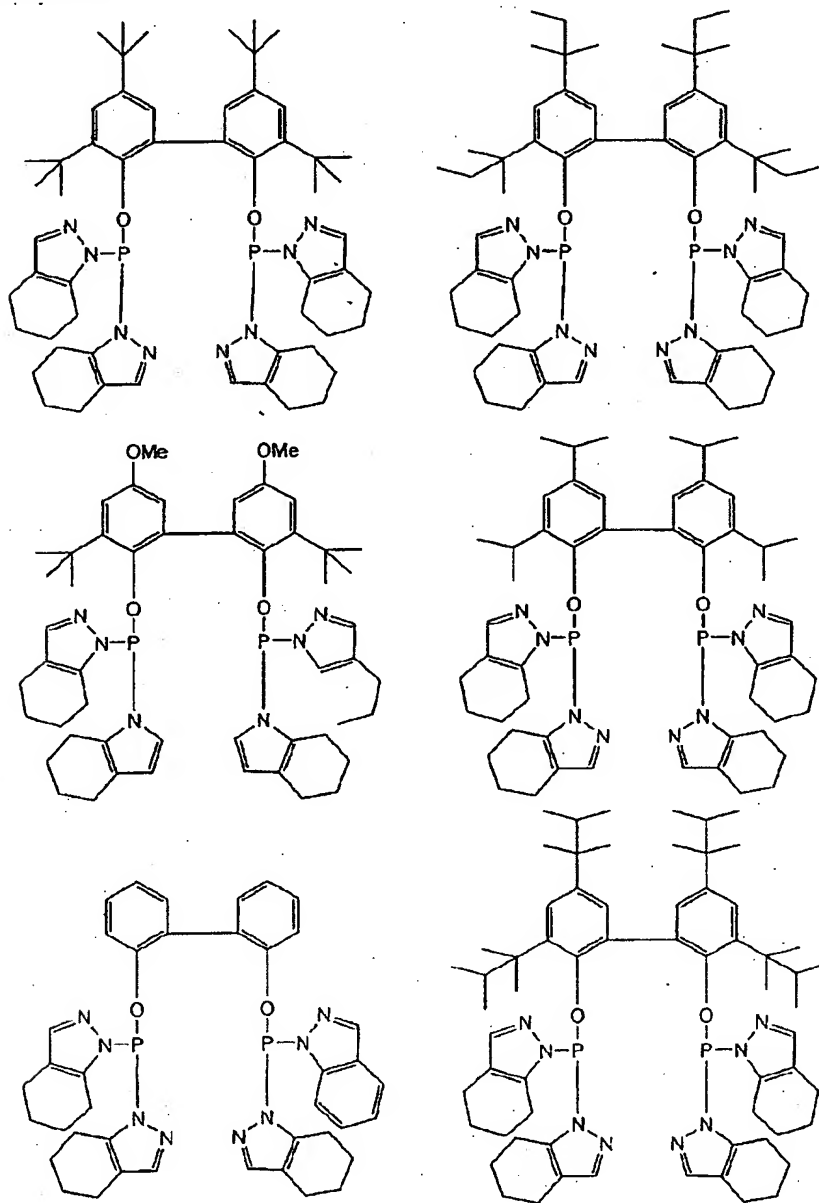


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[Formula 46]



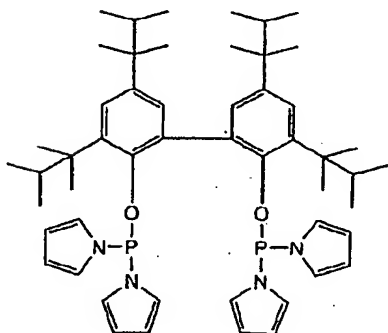
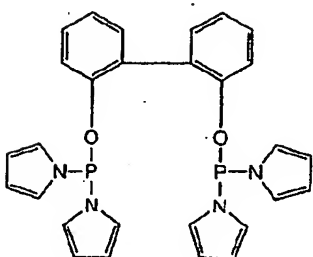
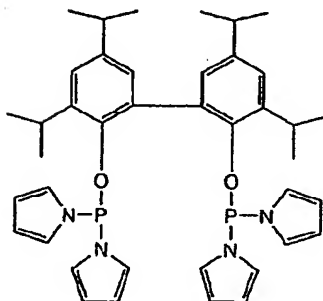
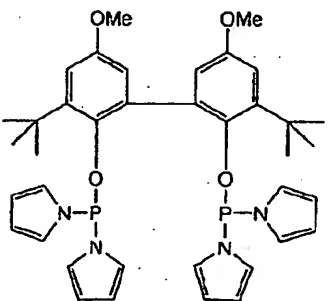
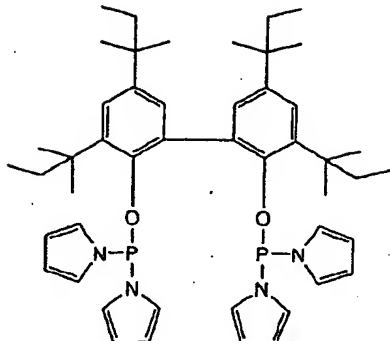
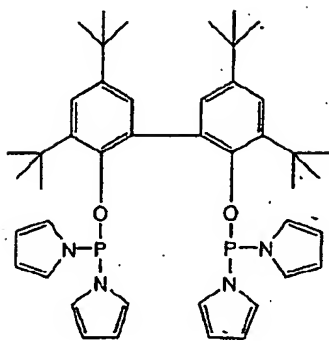


[0065]
[Formula 47]

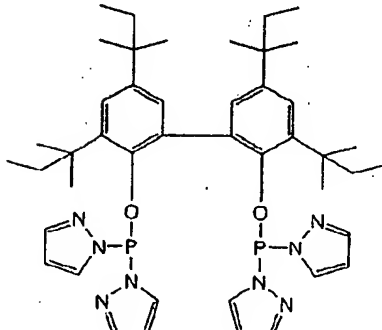
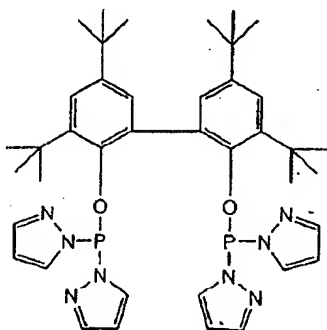


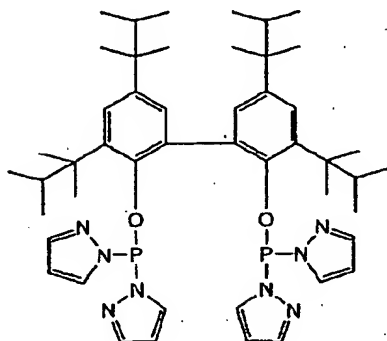
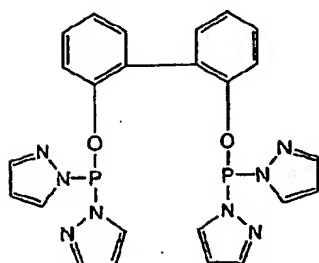
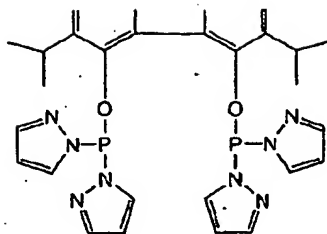
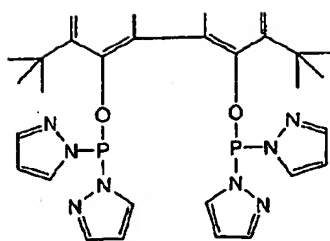
[0066]

[Formula 48]

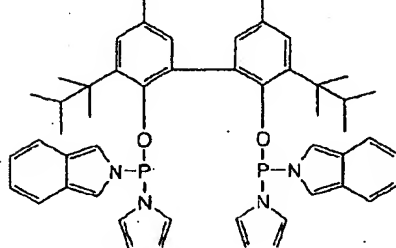
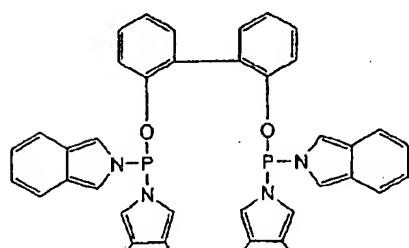
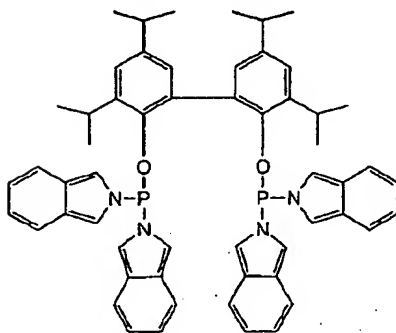
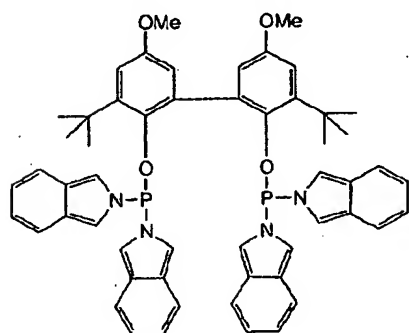
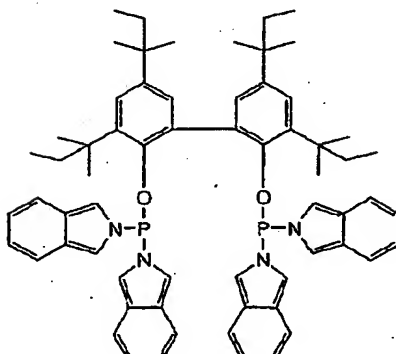
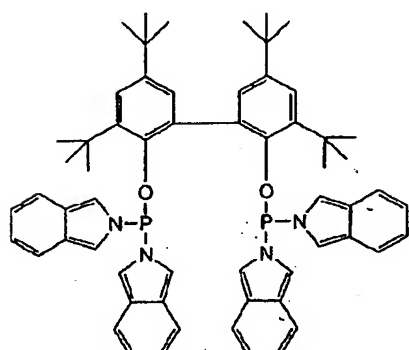


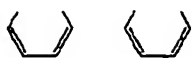
[0067]
[Formula 49]



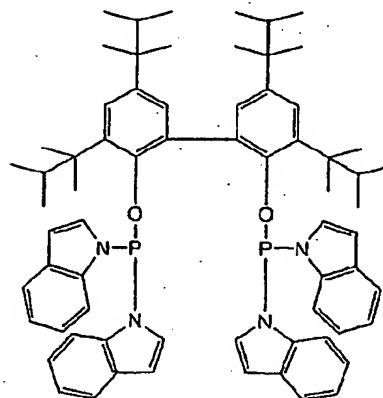
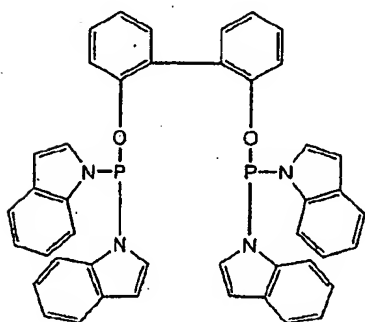
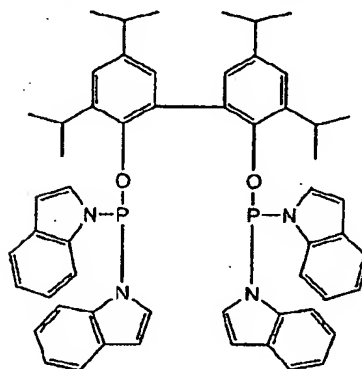
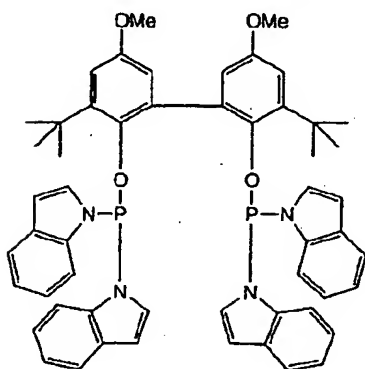
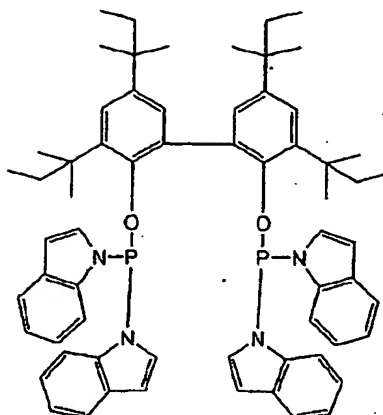
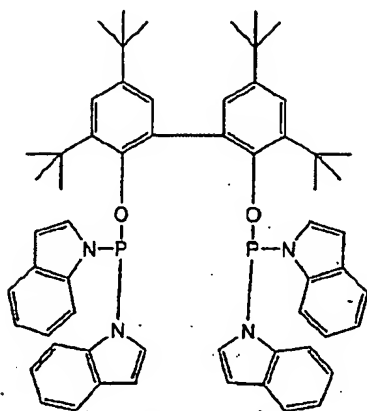


[0068]
[Formula 50]

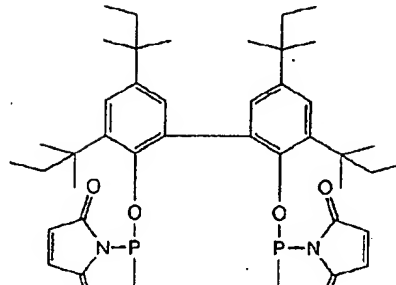
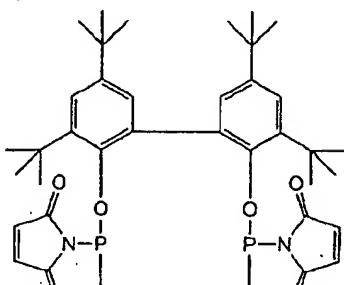


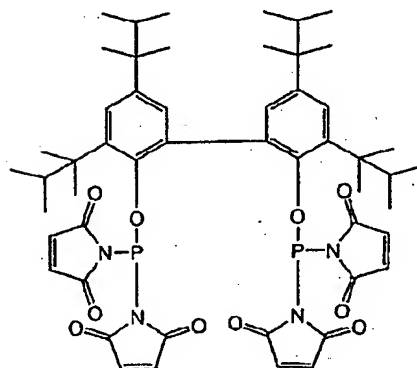
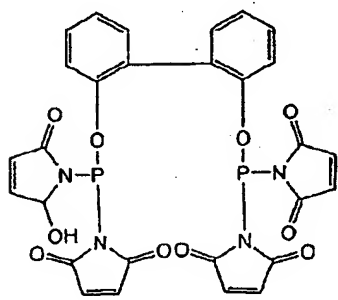
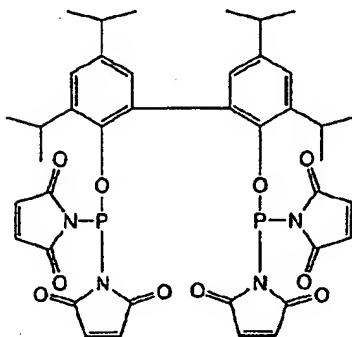
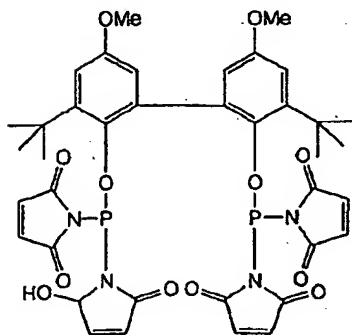
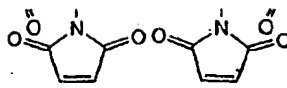
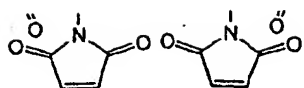


[0069]
[Formula 51]

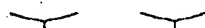
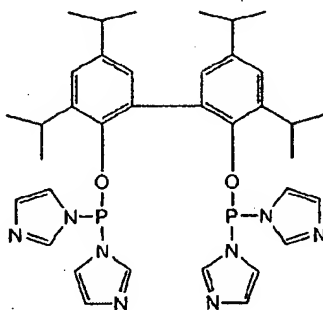
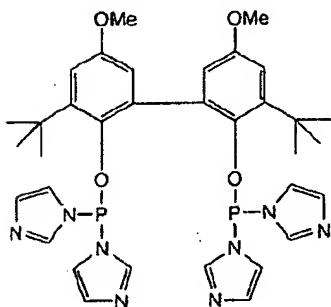
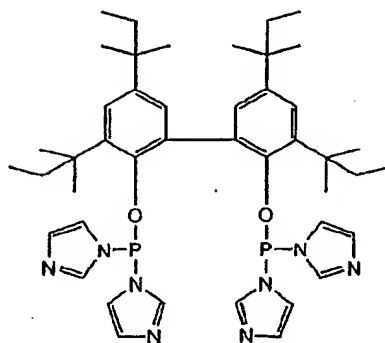
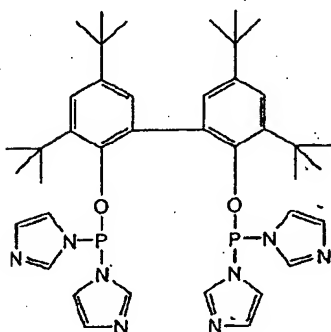


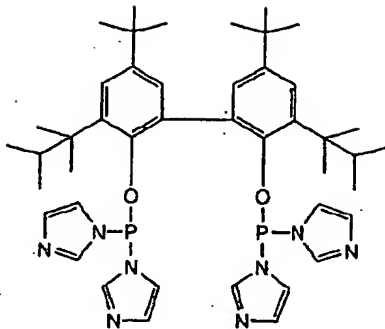
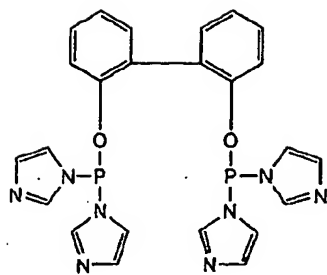
[0070]
[Formula 52]



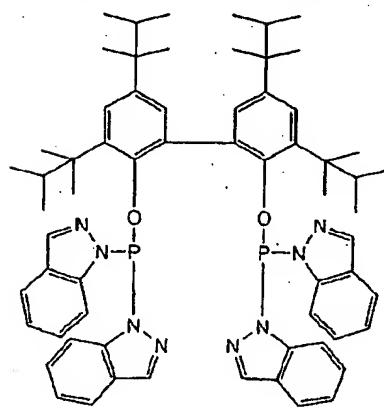
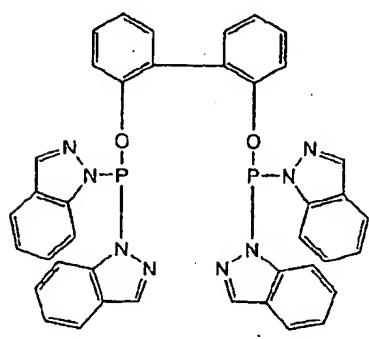
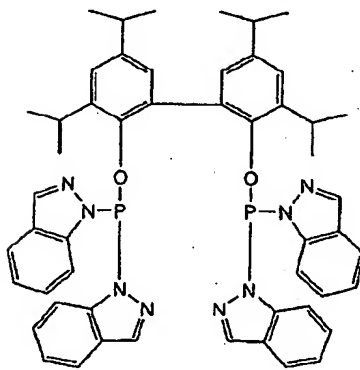
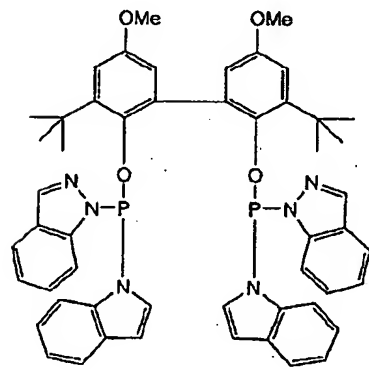
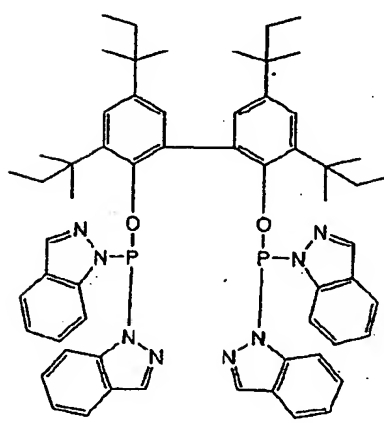
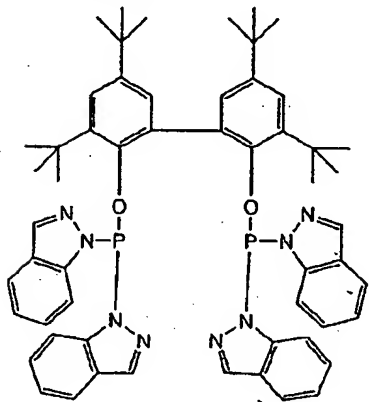


[0071]
[Formula 53]

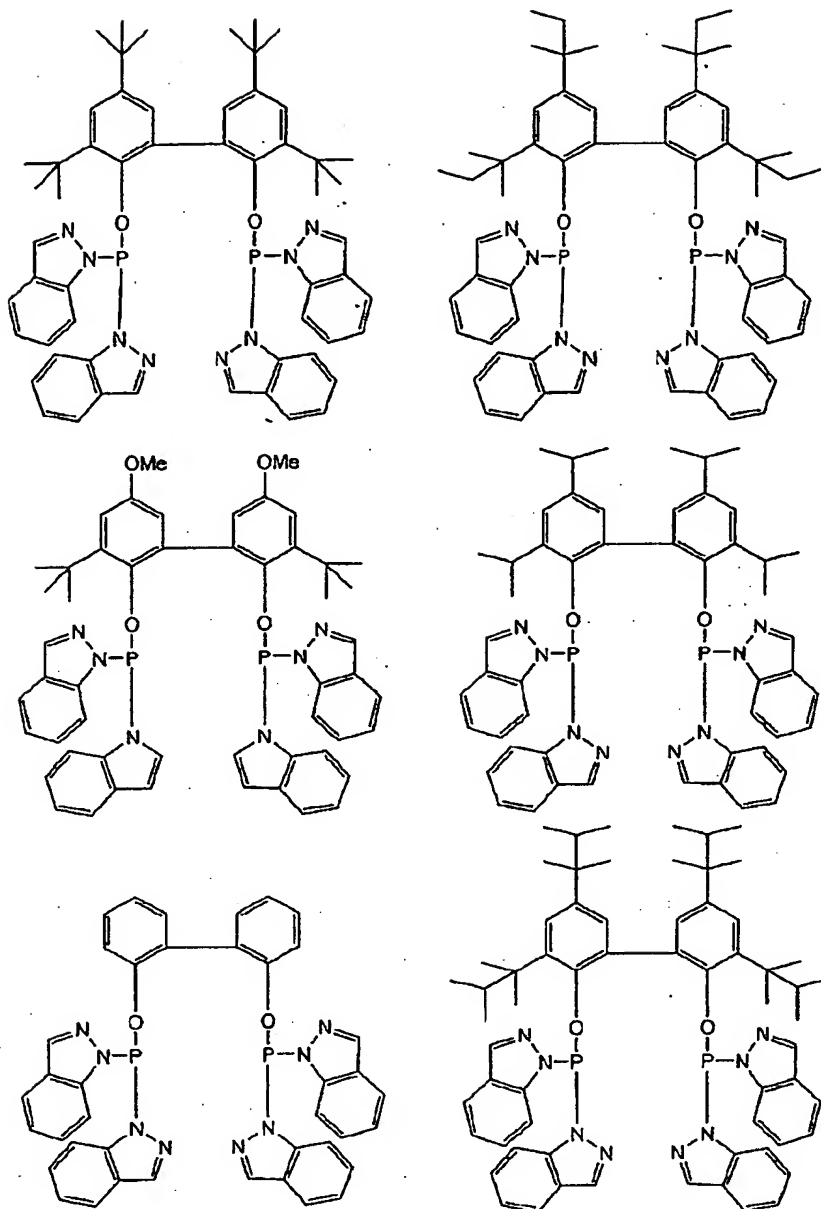




[0072]
[Formula 54]



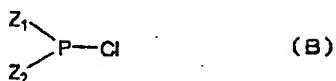
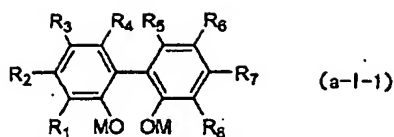
[0073]
[Formula 55]



[0074] As the general formula (A-a) of this invention, and (A-b) a synthesis method of 2 seat phosphorus compounds expressed, the method of using (1) chloro phosphine and the method of going via (2) poly (dihalogen-ized phospho lath) compound are mentioned. Taking the case of the case where the -Ar1-Ar2-machine of a general formula (A-a) is (a-I), a synthesis method is explained below. As a synthesis method of (1), it can compound, for example by the method of a publication to JP,10-45775,A, and is the following general formula (a-I -1) (R1-R8 of a general formula (a-I -1) and inside). it is R1-R8, and homonymy in a general formula (a-I), and M shows an alkali-metal salt or an alkaline-earth-metal salt The alkali-metal salt of 1 which has a substituent, respectively, the 1'-biphenyl -2, and a 2'-diol or alkaline-earth-metal salt expressed, and the following general formula (B) and/or (C) (Z1 -Z4 is homonymy with Z1 -Z4 of a general formula (A-a) among a formula, respectively.) The phosphorus compounds expressed can be prepared by making it contact.

[0075]

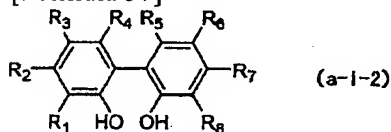
[Formula 56]



[0076] The screw aryene diol salt expressed with the above-mentioned general formula (a-I -1) is the following general formula (a-I -2) (R1-R8 in a general formula (a-I -2)). it is R1-R8, and homonymy in a general formula (a-I), respectively The 1 and 1'-biphenyl -2 and 2'-diol which are expressed and which have a substituent, respectively, Alkaline-earth-metal compounds, such as alkali metal compounds, such as n-BuLi, and Na, NaH, KH, or methyl-bromide magnesium, and ethyl-bromide magnesium, are compoundable by making it react under inert gas atmosphere, such as nitrogen, preferably among a solvent.

[0077]

[Formula 57]



[0078] Although it is enough if there are usually the two mols of the amount of the above-mentioned metallic compounds used to one mol of screw aryene diols expressed with a general formula (a-I -2), you may use it more than it by request. As a solvent, nitrogen-containing compounds and such mixture, such as a hydrocarbons [, such as ether, such as a tetrahydrofuran and diethylether a hexane, and toluene,], pyridine, triethylamine, N and N', and N'-tetramethylethylenediamine, are used suitably. Although reaction temperature can be suitably chosen in the range of -70 degrees C - the solvent boiling point, it can carry out between low eyes (room temperature), for example, -30 degrees C - 25 degrees C, at the time of the start of a reaction, and it can also adopt the method of raising to the boiling point of a solvent gradually after that. It is desirable to react from the point of reaction operation, using a tetrahydrofuran as a solvent, using n-BuLi, Na, or NaH as metallic compounds. Although reaction time can usually choose the range of 1 minute - 48 hours, about 24 hours is desirable from 10 minutes.

[0079] Although reaction mixture may be used for the compound shown by the general formula (a-I -1) as it is especially at the following process, without refining, it may process washing by the poor solvent, isolation by recrystallization operation, etc. beforehand. The phosphorus compounds shown by the general formula (B) and (C) Usually, a phosphorus trichloride (PCl3), Z1-H, Z2-H, Z3-H, or Z4-H (Z1 -Z4 is Z1 -Z4 and homonymy of a general formula (A-a) among a formula.) The heterocyclic compounds expressed are compoundable the bottom of existence of a base, or under absent by reacting preferably with the bottom of inert gas atmosphere, such as nitrogen, the inside of a solvent, or a non-solvent. Z1 Z2 Or Z3 Z4 Since the same phosphorus compounds are easily compoundable, they are desirable. Therefore, Z1 Z2, and Z3 and Z4 The case where both sides are the same to each is more desirable, and it is Z1, Z2, and Z3 especially. And Z4 The case of being the same is still more desirable.

[0080] As the above-mentioned base, inorganic bases, such as nitrogen-containing bases, such as a pyridine, a triethylamine, and a diethylamine, a sodium carbonate, and potassium carbonate, are illustrated. From the ease of reaction operation, a nitrogen-containing base is fond and is used. As for the amount of the base used, it is common to use two mols to PCl3 1 mol. if there are too few amounts of a base too in many -- unnecessary P(Z1) 2 (Z2), P(Z1) (Z2) 2, P(Z1) 3, and P(Z2) 3 etc. -- since the amount of byproductions of dichloro compounds, such as phosphorus compounds and Cl2 P (Z1), increases, it is not desirable

[0081] Although reaction temperature can choose arbitrary temperature, the method of carrying out at the temperature of a low eye, for example, 0-25 degrees C, (room temperature) at the time of the start of a reaction, and raising reaction temperature in the case where a nitrogen-containing

base is used, for example as a base, gradually after that is desirable. Although reaction time can choose the range of 48 hours from 1 minute, the reaction time of about 10 hours is desirable from 5 minutes. When reacting under existence of a base, although it usually exists in a reaction solution as a solid-state, this can remove preferably the salt of the hydrogen chloride and base which carry out a byproduction with advance of a reaction from the system of reaction by the method of filtering under inert gas atmosphere, such as nitrogen. When reacting under [of a base] absent, the method of removing the hydrogen chloride which carries out a byproduction from the system of reaction etc. is illustrated by carrying out the bubble of inert gas like nitrogen gas or argon gas into the system of reaction.

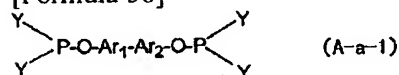
[0082] Although the chloro phosphines shown by the general formula (B) and (C) may be obtained as mixture with the above-mentioned unnecessary phosphorus compounds and a dichloro compound, it may progress to the following process, without dissociating especially with these. A method, distillation, etc. by the recrystallization which separates a general formula (B) and the phosphorus compounds of (C) from these by-products using aliphatic hydrocarbon solvents, such as a hexane and a heptane, as a method are mentioned.

[0083] The 2 seat phosphorus compounds of a general formula (A-a-1) can compound the compound of a general formula (a-I -1), and a general formula (B) and/or the compound of (C) among a solvent or under a non-solvent by making it contact 1 minute or more at the temperature of 25 degrees C or less. It is desirable to perform contact under inert gas atmosphere, such as nitrogen. The compound of a general formula (a-I -1), (B) Preferably the compound of (C) still more preferably 5 degrees C or less And/or, 0 degree C or less, It mixes at the temperature of -30 degrees C or less most preferably, and 1 minute or more, after maintaining the temperature for 3 minutes to 60 minutes preferably, the target screw phosphite compound is compoundable by the method of raising temperature gradually and going. As a climbing speed of temperature, although it can choose suitably in between for part [for 0.1 degrees-C/-], and 20-degree-C/, 0.5-degree-C a part for /-, and 10-degree-C speed for /are desirable. As a reaction solvent, nitrogen-containing compounds, such as a hydrocarbons [, such as ether, such as a tetrahydrofuran diethylether, and a dioxane, a hexane and toluene,], pyridine, triethylamine, N and N, N', and N'-tetramethylethylenediamine, and such mixture can be used. Although it is desirable to use the minimum amount required for the dissolution of the specified substance to generate as for the amount of a solvent, it does not interfere, even if it uses the amount beyond it.

[0084] Next, how to go via (2) poly (dihalogen-ized phospho lath) compound is explained. As a synthesis method of (2), are compoundable by the method of a publication to JP,2000-53688,A, for example. The multi-seat organic phosphorus compound of the following general formula (A-a-1), Z1-H, Z2-H, Z3-H, or Z4-H (Z1 -Z4 is Z1 -Z4 and homonymy of a general formula (A-a) among a formula.) It compounds by making the heterocyclic compounds expressed react.

[0085]

[Formula 58]



[0086] (-Ar1-Ar2- is the same as that of what was expressed with the general formula (A-a) among a formula, and Y expresses a halogen atom.) Z1-H used by this invention, Z2-H, Z3-H, and Z4-H can use the same thing as the heterocyclic compounds used in the process which compounds the formula (B) mentioned above or the phosphorus compounds of (C).

[0087] Although coexistence of a base is not indispensable in manufacturing the 2 seat phosphorus compounds which use as a raw material the poly (dihalogen-ized phospho lath) compound expressed with a general formula (A-a-1), and are expressed with a general formula (A-a), since a reaction advances easily, under the coexistence, it is advantageous. As a base, a lithium, sodium, and a potassium are illustrated as an alkali metal. As the second class amine which magnesium and calcium are illustrated as an alkaline earth metal, and has the hydrocarbon group of carbon numbers 1-22 As the third class amine which a diethylamine and diisopropylamine are illustrated and has the hydrocarbon group of carbon numbers 1-22 A triethylamine, tripropylamine, a triisopropyl amine, Tributylamine, a TORIISO butylamine, a trioctylamine, N,N-dimethylaniline, 1-methyl pyrrolidine, 1-methyl piperidine, a 1-MECHIRU 2-pyrrolidone, A pyridine, 2-picoline, 3-picoline, 3-picoline, and 1-methyl pyrrole are mentioned as a 1-MECHIRU 2-piperidone and a heterocycle formula aromatic compound, and alkali metal or the third class amine is suitable especially.

[0088] Although there is no limit in order of mixture of each component at the time of making the poly (dihalogen-ized phospho lath) compound, Z1 H-Z4H, and a base react, when using alkali

metal and alkaline earth metal as a base, Z1 H-Z4H, When it is advantageous at the point of giving yield [made / better / for the poly (dihalogen-ized phospho lath) compound to react continuously] and uses the second class amine as a base after making a base react After making a base react after mixing the poly (dihalogen-ized phospho lath) compound with Z1 H-Z4H, or mixing Z1 H-Z4H and a base, it is advantageous at the point of giving yield [made / better / for the poly (dihalogen-ized phospho lath) compound to react continuously]. although there is no limit in mixed sequence when using the heterocycle formula aromatic compound which does not have the third class amine or an active hydrogen atom -- beforehand -- Z1 H-Z4H -- having mixed Z1 H-Z4H and the base, having continued and having made it or more advantageous for the poly (dihalogen-ized phospho lath) compound to react

[0089] the number of the halogen atoms which especially the amount of the base used to be used is not restricted in case this invention is reacted, and were usually combined with the Lynn atom of the poly (dihalogen-ized phospho lath) compound -- receiving -- 0.01-mol twice to 10000 it chooses in the twice [mol] as many range as this -- having -- desirable -- 0.1 Mol twice to 100 mol twice -- it is especially chosen out of one-mol twice in the twice as many ten-mol range as this preferably

[0090] If required, an inactive solvent can be made to exist in a reaction, although use of a reaction solvent is not indispensable in case this invention is reacted. The example of a desirable solvent Aliphatic hydrocarbon, such as a hexane, a heptane, and an octane, Aromatic hydrocarbons, such as toluene, a xylene, and a dodecylbenzene, an acetone, Ketones, such as a diethyl ketone and a methyl ethyl ketone, diethylether, Ether, such as dibutyl ether, a tetrahydrofuran, and a dioxane, Ester, such as ethyl acetate, a triethylamine, tripropylamine, The third class amines, such as a 1-MECHIRU 2-pyrrolidone and a 1-MECHIRU 2-piperidone, The mixture which carries out a byproduction is mentioned at the time of manufacture of heterocycle formula aromatic compounds, such as a pyridine and 2-picoline, and the poly (dihalogen-ized phospho lath) compound, and the poly (dihalogen-ized phospho lath) compound itself and Z1 H-Z4H can also be used as a solvent.

[0091] the number of the halogen atoms which especially the amount of Z1 H-Z4H used to be used is not restricted in case this invention is reacted, and were usually combined with the Lynn atom of the poly (dihalogen-ized phospho lath) compound -- receiving -- 0.01-mol twice to 10000 it chooses in the twice [mol] as many range as this -- having -- desirable -- 0.1 Mol twice to 100 mol twice -- it is especially chosen out of one-mol twice in the twice as many ten-mol range as

[0092] the reaction temperature at the time of reacting this invention is chosen from -78 °C in 80 degrees C -- having -- desirable -- 30 degrees C from -50 °C -- especially -- desirable -- the range of -30 °C to 10 degrees C -- it is most preferably chosen in -15 to 5 degrees C

[0093] Although the removal of an impurity [activity / a reaction] which may be mixed in the solvent used for this invention and all chemicals is not indispensable, since the way of yield which removed improves, it is economically advantageous and desirable.

[0094] Although there is no limit in the synthesis method of the 2 seat phosphorus compounds which can apply this invention, even if it makes Z1 H-Z4H react simultaneously to the poly (dihalogen-ized phospho lath) compound of a general formula (A-a -1) although you may make it react gradually -- Z1 and Z2 on -P (Z1) (Z2) machine things -- the gradual synthesis method is suitable for the purpose which compounds 2 seat phosphorus compounds more advantageously That is, when making heterocyclic compounds react, one halogen atom of each dihalogen-ized phospho lath machine is preferentially replaced by the poly (dihalogen-ized phospho lath) compound expressed with a general formula (A-a -1). Therefore, it is Z1 on -P (Z1) (Z2) machine respectively by making Z2H of the too same number as the Lynn atomic number react, after making Z1H of the same number as the Lynn atomic number react. It is possible to compound the 2 seat phosphorus compounds with which Z2 °C's differ. Since each Lynn atom has chirality while being used for catalytic reaction as a ligand, the 2 seat phosphorus compounds compounded by this method fit the use to the use to an asymmetric-catalyst reaction, and the optical resolution of an asymmetrical compound as a ligand. Moreover, it is suitable also for the use as an additive to polymeric materials.

[0095] The poly (dihalogen-ized phospho lath) compound expressed with a general formula (A-a -1) can be compounded by various reactions. For example, being obtained by the reaction of a corresponding polyhydroxy compound and a corresponding phosphorus trichloride like bisphenols is indicated by DE19513541. moreover, A.A.Kutyrev °C -- it has reported that corresponding dichlorophosphite is obtained by the reaction of 1 and 4-benzoquinone and a phosphorus trichloride (Zh. Obshch. Khim. 62(8), 1768-1771 (1992)) Furthermore, the ring closure in a molecule which is good yield about the poly (dihalogen-ized phospho lath) compound, and is side reaction simultaneously can be suppressed by adopting the method to

which the hydrogen halide expressed with the poly (screw (JIHIDOROKARUBIRUAMINO) phospho lath) compound and HY is made to react as indicated by JP,2000-53688,A.

[0096] the synthesis method mentioned above -- following -- the -Ar1-Ar2-machine of a general formula (A-a) -- the case of the 2 seat phosphorus compounds of (a-II), and the -Ar3-Ar4-machine of a general formula (A-b) -- or (b-I) (b-II) is compoundable similarly about the case of 2 seat phosphorus compounds Also in the method of of (1) and (2) mentioned above, the synthesis method of (1) is more desirable. a general formula (A-a) -- and (A-b) is mentioned for the method by column expansion (chromatography), the method by ****, the method by recrystallization, etc. as the refining method of 2 seat phosphorus compounds The method of using silica gel, an oxidization alumina, etc. as a bulking agent as a method by column expansion is mentioned. Moreover, as an expansion solution of a column, halogenated hydrocarbons, such as ester, such as aromatic hydrocarbons, such as aliphatic hydrocarbon, such as ether, such as a tetrahydrofuran and a dioxane, a hexane, and a heptane, toluene, and a xylene, ethyl acetate, and methyl acetate, chloroform, and a dichloromethane, are mentioned, a single solvent or two or more kinds of solvents are mixed, and these solutions are used so that it may be suitable for refining of the specified substance.

[0097] As the refining method by ****, moreover, after the end of a 2 seat Lynn composition reaction, according to **, Or after removing the hydrochloride of the salt which carried out the byproduction by polar solvents, such as water, for example, a metal chloride, (MCl), and a nitrogen-containing compound from a reaction solution, By carrying out evaporation **** of the solution and agitating the residue in solvents, such as alcohols, such as ketones, such as aliphatic hydrocarbon, such as an acetonitrile, a hexane, and a heptane, an acetone, and a diethyl ketone, a methanol, and ethanol The specified substance can be refined by the method of dissolving discard in a solvent, without dissolving the specified substance in these solvents.

[0098] As the refining method by recrystallization, after the end of the synthetic reaction of 2 seat phosphorus compounds, After removing the hydrochloride of a ** exception or the salt which carried out the byproduction by polar solvents, such as water, for example, a metal chloride, and a nitrogen-containing compound from a reaction solution, After making it dissolve in the solvent of the minimum amount which carries out evaporation **** of the solution and may dissolve the residue, After dissolving in the method by cooling, and the solvent which may dissolve the residue, The insoluble or refractory solvent of the 2 seat phosphorus compounds of the specified substance is added, a solid-state is deposited by the method by cooling by request etc., a solid-state is separated by methods, such as filtration, and the method of washing with a solvent with a still more insoluble solid-state etc. is mentioned. As a solvent with meltable 2 seat phosphorus compounds, ether, such as aromatic hydrocarbons, such as benzene, toluene, and a xylene, a tetrahydrofuran, and a dioxane, is mentioned, and alcohols, such as ketones, such as aliphatic hydrocarbon, such as a hexane besides an acetonitrile and a heptane, an acetone, and a diethyl ketone, a methanol, and ethanol, are illustrated as a refractory solvent.

[0099] In this invention, it is performing a hydroformylation reaction using the new 2 seat phosphorus compounds mentioned above, and it becomes possible to fill simultaneously a high reaction rate and the selectivity of the outstanding purpose product. In the hydroformylation method of this invention, if it is the organic compound which has at least one olefin nature double bond in a molecule as an olefin nature compound used as a reaction raw material, there will be especially no limit. Specifically Ethylene, a propylene, a butene, a butadiene, a pentene, A hexene, a hexadiene, an octene, an OKUTA diene, decene, hexa decene, Octadecene, IKOSEN, DOKOSEN, styrene, an alpha methyl styrene, A cyclohexene and propylene - butene mixture, 1-butene - 2-butene - isobutylene mixture, Low-grade olefin mixture, such as 1-butene - 2-butene isobutylene - butadiene mixture, Olefins, such as olefin oligomer isomer mixture like the dimer of low-grade olefins, such as a propylene, n-butene, and an isobutylene, - a tetramer Acrylonitrile, allyl alcohol, 1-hydroxy - 2, 7-OKUTA diene, 3-hydroxy - Polar-group substitution olefins, such as 1, 7-OKUTA diene, oleyl alcohol, the 1-methoxy -2, 7-OKUTA diene, a methyl acrylate, a methacrylic-acid methyl, and a methyl olcate, are mentioned. In this invention, the olefin nature compound which does not have a polar functional group is desirable, an alpha olefin is more desirable, and a propylene is the most desirable also in having mentioned above.

[0100] As the 8th group metallic compounds used as the catalyst of a hydroformylation reaction, or its precursor The hydride, the halogenide, the organic acid chloride, the inorganic-acid salt, the oxide, a carbonyl compound, an amine compound, an olefin coordination compound, a phosphine coordination compound, or a phosphite coordination compound of the 8th group metal etc. is usable. For example, a ruthenium trichloride, TETORAAMMINHIDOROKISO chloro ruthenium chloride, Ruthenium compounds, such as a dichloro tris (triphenyl phosphine) ruthenium, Osmium compounds, such as palladium compounds, such as acetic-acid palladium and a

palladium chloride, and a 3 chlorination osmium, Iridium compounds, such as 3 iridium chlorides and an iridium carbonyl, a platonic acid, Platinum compounds, such as a sodium hexachloroplatinate and the second platonic-acid potassium, Cobalt compounds, such as a dicobaltoctacarbonyl and stearin acid cobalt, A rhodium trichloride, a nitric-acid rhodium, an acetic-acid rhodium, and Rh (acac) (CO)₂, [Rh (OAc) (COD)] -- 2 and Rh₄ (CO)₁₂ and Rh₆ (CO)₁₆ and HRh (CO) (PPh₃) -- three -- [Rh (CO)₂ (OAc)] -- 2 and [Rh (micro-S (t-Bu)) (CO)₂] -- 2 -- [RhCl (COD)], although the rhodium (acac -- acetylacetonate machine -- OAc -- acetyl group -- Ph expresses phenyl group and, as for t-Bu, COD expresses 3rd butyl for 1 and 5-cyclo-octadiene, respectively) compound of 2 etc. is mentioned It is not necessarily limited to these. In this invention, especially, cobalt, a rhodium, and a ruthenium are desirable and a rhodium is the most desirable.

[0101] In this invention method, 2 seat phosphorus compounds can make the above-mentioned 8th group metallic compounds and an above-mentioned complex able to form beforehand, and can be used. The 8th group metal complex containing 2 seat phosphorus compounds can be easily prepared by the well-known complexing method from the compound of the 8th group metal, and these 2 seat phosphorus compounds. Moreover, depending on the case, the 8th group metallic compounds and the aforementioned 2 seat phosphorus compounds are supplied to a hydroformylation reaction-zone region, and a complex can be made to be able to form and it can also use there. Although especially the amount of the 8th group metallic compounds used has the limitation which is not limited and is taken into consideration from catalytic activity, economical efficiency, etc., in this invention, 0.05mg - 5g of concentration in a hydroformylation reaction-zone region is usually preferably chosen from the range of 0.5mg - 1g to an olefin nature compound or 1l. of reaction solvents by metal atom conversion.

[0102] In this invention, especially the amount of the 2 seat phosphorus compounds used is not restricted, and it is suitably set up so that a desirable result may be obtained to the activity of a catalyst, and selectivity. Usually, about 0.001-500 mols per one mol of 8th metal are preferably chosen from the range of 0.1-100 mols. If required, an inactive solvent can be made to exist in a hydroformylation reaction, although use of a reaction solvent is not indispensable in performing a hydroformylation reaction. As an example of a desirable solvent, the high boiling point component which carries out a byproduction to hydroformylation reaction time, such as ester, such as ether, such as ketones, such as aromatic hydrocarbons, such as toluene, a xylene, and TODESHIRU benzene, an acetone, a diethyl ketone, and a methyl ethyl ketone, a tetrahydrofuran, and a dioxane, ethyl acetate, and G n-octyl phthalate, and an aldehyde condensation product, or the olefin nature compound which is a reaction raw material is mentioned.

[0103] the reaction condition for performing the hydroformylation method of this invention is the same as that of what was usually alike and was used conventionally, and 15-200 degrees C of reaction temperature are usually preferably chosen from the range of 50-150 degrees C -- having - CO partial pressure and H₂ a partial pressure -- usually -- it is especially chosen out of the range of one to 50 atmospheric pressure preferably 0.1 to 100 atmospheric pressure 0.001 to 200 atmospheric pressure the mole ratio (H₂ / CO) of hydrogen and a carbon monoxide -- usually -- 10 / 1 - 1/10 -- it is preferably chosen from the range of 1 / 1 - 1/6 As a method of a hydroformylation reaction, either a continuous method or a batch method can be held in an agitated type reaction vessel or a bubbling-tower type reaction vessel.

[0104] In the hydroformylation system of reaction using the general formula (A-a) or (A-b) the new 2 seat phosphorus compounds shown of this invention, after separating the generated aldehyde by methods, such as distillation, the hydroformylation reaction of an olefin nature compound can be again performed using the recovery liquid containing this 8th group metal and 2 seat phosphorus compounds. Furthermore, in case an olefin nature compound is continuously converted into an aldehyde, a hydroformylation reaction vessel can also be made to circulate through the remaining reaction mixture which separated a part or all of an aldehyde that is generated continuously as catalyst liquid. After it presents a hydrogenation reaction with the aldehydes obtained by the method of this invention as they are or it dimerizes according to a well-known method, for example, USP5550302 and USP5667644, it becomes possible [manufacturing the suitable alcohol for plasticizers, such as a normal butanol, 2-ethyl hexanol, and nonyl alcohol,] by presenting a hydrogenation reaction.

[Translation done.]

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EXAMPLE

[Example] Next, although an example explains the concrete mode of this invention still in detail, this invention is not limited by the following examples unless the summary is exceeded.

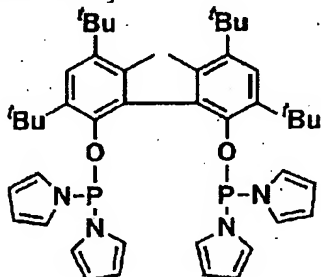
[0106] Example -1 (composition of tetrapod pyrrolyl screw phosphite (ligand 1))

The toluene (80ml) solution of the pyrrole (3.89g, 58mmol) distilled and built in the toluene (100ml) solution of PCl_3 (g [3.99], 29mmol) and a triethylamine (8.82g, 87mmol) was dropped at 0 degree C. When heated at 60 degrees C for 2 hours, it was checked in ^{31}P -NMR that the JIPIRORIRU chloro phosphine is generating with 83% of selectivity (δ 104.4). The filtrate which filtered the salt was condensed to 50ml. Separately, the hexane solution of n-BuLi (29mmol) was mixed at 0 degree C, the heating reflux of the THF solution (40ml) of 3, 3', 5, and 5'-tetrapod-tert-butyl -6, the 6'-dimethyl -2, and 2-biphenol (6.37g, 14.5mmol) was carried out after that for 1.2 hours, and Li salt of biphenol was obtained. Li salt of biphenol was dropped at the toluene solution of a JIPIRORIRU chloro phosphine at 0 degree C. The salt was carried out the ** exception after the reaction, and filtrate was condensed. As a result of carrying out isolation refining of the residue which remained with a silica gel column chromatography (developing solution : toluene : hexane = 1:5), 2.13g (19%) of ligands 1 of the structure shown below was obtained.

mp 215.6-216.3 degree-C ^{31}P -NMR (CDCl_3) δ 99.781 H-NMR (CDCl_3) δ 7.37 (s, 2H), 6.81 (m, 4H), 6.68 (m, 4H), 6.20 (m, 4H), 6.15 (m, 4H), 1.94 (s, 6H), 1.29 (s, 18H), 1.06 (s, 18H)

[0107]

[Formula 59]



配位子 1

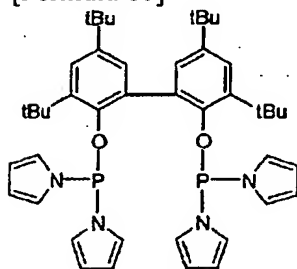
[0108] The structure of the above-mentioned ligand 1 was checked using Lynn ^{31}P -nuclear-magnetic-resonance spectrophotometric analysis, proton nuclear-magnetic-resonance spectrophotometric analysis (equipment is the unity 300 type made from Varian), or the elemental-analysis method.

[0109] The example -1 (hydroformylation reaction using the ligand 2) of a reaction 2 seat Lynn ligand 2 shown the bottom of the dried nitrogen atmosphere, and in the glassware at 19.7mg 2 and the following (OAc (cod)) The toluene (214.4mg and 55ml) which carried out deaeration dehydration, and the 5ml heptane (internal standard of the gas-chromatography analysis after a reaction) which carried out deaeration dehydration were added, and the uniform solution was prepared. Then, dryness nitrogen replaced the often dried vertical stirring type autoclave made from stainless steel of 200ml of content volume 3 times, and under nitrogen atmosphere, the above-mentioned solution was pressed fit in the autoclave by nitrogen pressure, and was sealed. After pressing the 4.5 moreg propylene fit in the autoclave and sealing it, the temperature up of auto REBU was carried out to 70 degrees C. At this time, internal pressure was 4 kg/cm². Then, although synthesis gas ($\text{H}_2:\text{CO}=1:1$) was introduced in auto REBU and the hydroformylation reaction of a propylene was started, synthesis gas is introduced through a

secondary-pressure regulator from a pressure accumulator, and it was made forkg [of the total pressure in an autoclave / 9 /] to always be set to 2 cm among a reaction. 5.0 hours after, the failure of pressure of a pressure accumulator was lost mostly, and ended the reaction. The autoclave was cooled to the room temperature after the reaction end, the uptake of the gaseous phase and the liquid phase in an autoclave was carried out, and component analysis of each was carried out using the gas chromatography. Consequently, 93.7% and the C4-aldehyde yield of the invert ratio of a propylene were 91.9%, and the ratio (n/i ratio) of n-butyraldehyde of the specified substance and i-butyraldehyde of a by-product in a C4-aldehyde was 25.5. Moreover, the velocity constant for which it asked from the rate of the failure of pressure of a pressure accumulator was 0.53h⁻¹. Moreover, although the signal based on a Rh-P complex in the signal based on [as a result of performing 31 P-NMR measurement of reaction mixture] the ligand of 100.8 ppm isolation was observed by 138-142 ppm again, other than this, the signal based on decomposition of a ligand was not observed.

[0110]

[Formula 60]



配位子 2

[0111] The example -2 (hydroformylation reaction using the ligand 1) of a reaction
The hydroformylation reaction of a propylene was carried out by the same method using the 2 seat Lynn ligand 1 compounded in the 222.6mg above-mentioned example -1 instead of the 214.4mg ligand 2 used in the example -1 of a reaction except it. Reaction time was 2.0 hours. As a result of performing same analysis, 96.6% and the C4-aldehyde yield of the invert ratio of a propylene were 94.8%, and the n/i ratio in a C4-aldehyde was 100.9. Moreover, the velocity constant was 2.16h⁻¹. moreover, the signal based on [as a result of performing 31 P-NMR measurement of reaction mixture] the ligand of 99.5 ppm isolation -- moreover, although the signal based on a Rh-P complex was observed by 137.7 ppm (d, 2 JRh-P=209.8Hz), other than this, the signal based on decomposition of a ligand was not observed

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